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ERRATA

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Owing to the fact that Dr. Pedersen did not read proof for his three papers appearing in this issue, the following changes should be made:

Page 560. For (14) in the 27th line, read (11).

Page 561. For ϕ in the 8th line, read φ.

Page 565. For $\beta = \dfrac{0.4343K}{\varphi(a + K^2)}$ read $\beta = \dfrac{0.4343K}{\varphi(a + K)^2}$

Page 566. For 0.5005 in the 4th line of the first column of table 4, read 0.05005.

Page 567. For 32.7 in the last column of table 8, read 23.7.

For "acid" in the heading of table 8, read "and."

Page 584. Formula 9 should read $\dfrac{k_A}{p} = G\left(\dfrac{q}{p} K_A\right)^{\alpha}$

Page 585. For $\dfrac{g_0}{q_-}$ in formula 14, read $\dfrac{g_0}{g_-}$.

For $\dfrac{\pi_{BH^+,R}}{\pi_{BH,R}}$ in the formula following formula 14, read $\dfrac{\pi_{BH^+,R}}{\pi_{BH,R^-}}$

Page 589. For "body" in the 13th line, read "both."

Page 593. For $\Sigma\pi_{A,I^-}(A)$ in the middle one of the three formulas following formula 26, read $\Sigma\pi'_{A,I^-}(A)$.

For π'_{A,I^-} in the 24th line, read π''_{A,I^-}.

Page 596. The formula in the middle of the page should read

$$\underset{(RH')}{CH_3\cdot CO\cdot CH_3} \rightleftarrows \underset{(IH_2^{+\prime})}{CH_3\cdot(\overset{+}{C}{:}OH)\cdot CH_3} \rightleftarrows \underset{(SH')}{\overset{-}{C}H_2\cdot(C{:}\overset{+}{O}H)\cdot CH_3} \rightleftarrows \underset{(SH'')}{CH_2{:}COH\cdot CH_3} \quad (30)$$

Page 598. For $O{:}C\cdot CH_2 \rightleftarrows$ in formula 33, read $O{:}C\cdot CH_2 \rightleftarrows$.

Page 600. For **1927** in reference 22, read **1926**.

Page 602. The fourth formula should read

$$(H^+) = (H^+)_0 + \kappa\frac{x}{4}$$

Page 609. For k_{HB} just below the heading of table 5, read K_{HB}.

Page 618. For $G^* \times 10$ in the heading of the last column of table 14, read $G^* \times 10^2$.

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THE PRECISION AND ACCURACY OF A PHOTOELECTRIC METHOD FOR COMPARISON OF THE LOW LIGHT INTENSITIES INVOLVED IN MEASUREMENT OF ABSORPTION AND FLUORESCENCE SPECTRA

F. F. ZSCHEILE, JR.,[1] T. R. HOGNESS, AND T. F. YOUNG

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Received May 27, 1933

The usual photographic methods for measurement of continuous absorption spectra of solutions are not satisfactory for accurate measurement of extinction coefficients; the greatest care is necessary to obtain an accuracy of even 5 per cent (1). Visual methods are affected by inaccuracies of the eye and are practically limited to the visible region of the spectrum.

A more precise method, which involves the use of a monochromator and a photoelectric cell, avoids the errors of both the photographic plate and the eye. The photoelectric current measurement is not affected by uncertain amplification factors when an electrometer and a high resistance leak are employed. Because of the high sensitivity and precision of the photocell and electrometer, very narrow regions of a continuous spectrum may be used. Although the use of a line source permits precise definition of wave lengths, the usual intensity fluctuations make it less desirable for this photoelectric method. Because its intensity may be conveniently controlled, a continuous source is preferable when the resolution of the monochromator and the precision of current measurements can be made sufficiently great. Furthermore, the continuous spectrum does not display the abrupt changes in intensity with wave length which characterize line spectra, and it permits the convenient use of arbitrarily selected wave lengths.

Although the essentials of this method are not new, we have not found a detailed description of the complete assembly, its operation, errors, and precision. The method is especially suitable for the detection of compounds and for quantitative analysis of complex mixtures, particularly the biological pigments, such as the chlorophylls. It will undoubtedly become more generally used.

[1] National Research Fellow, 1931–1933.

DESCRIPTION OF EXPERIMENTAL EQUIPMENT

Figure 1 is a diagram of the entire experimental system. Light from source S, after being condensed by a lens (focal length 12 cm.; diameter 4.5 cm.) is focused on slit 1 of the monochromator. By adjustment of the wave length scale, the prism is so rotated that light of the desired wave length will travel from slit 1 to slit 2, providing lenses l_1 and l_2 are in proper focus. Between slit 2 and the photoelectric cell P, is a camera shutter with a 2-cm. diaphragm opening. The shutter, set for "time," is opened and closed by a cable release which reaches to the telescope.

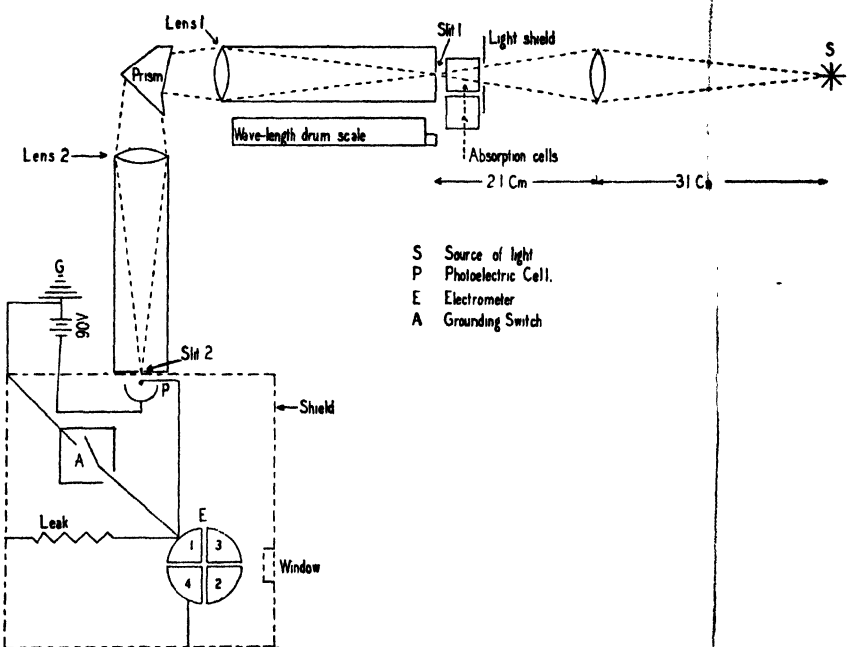

FIG. 1. INTENSITY COMPARISON SYSTEM

Across P is impressed a potential of 90 volts from radio "B" batteries. The photoelectric current, caused by light from slit 2, is measured by means of a quadrant electrometer. The vane deflections are determined by means of a telescope and scale, which in our case is 2.5 meters from the electrometer mirror. After calibration of the electrometer, deflections are accurate measures of the photoelectric currents, and hence of the relative intensities of the light of any wave length entering slit 1.

In figure 2 is a diagram of the electrical circuit used to measure the small currents involved. The electrometer, photocell, ground leak, and grounding switch are enclosed completely in a tinned iron case, which is grounded

and acts as a shield against stray electric fields. The case is lined on the inside with loose cotton felt 5 mm. thick, which diminishes temperature fluctuations to which electrometers, especially the Compton, are sensitive. Around the case, on the outside, is a hood of black felt which helps to keep out stray light. All wires enter the case through Bakelite insulators. The case and all of its contents are placed on a concrete pillar, which in turn rests on a 1 cm. rubber pad on a larger concrete pillar extending into the ground.

When 90 volts are impressed on P by the closing of switch B, the photoelectric current flows to the ground if A is closed. The grounding switch A is insulated with paraffin and has platinum contacts. When A is opened,

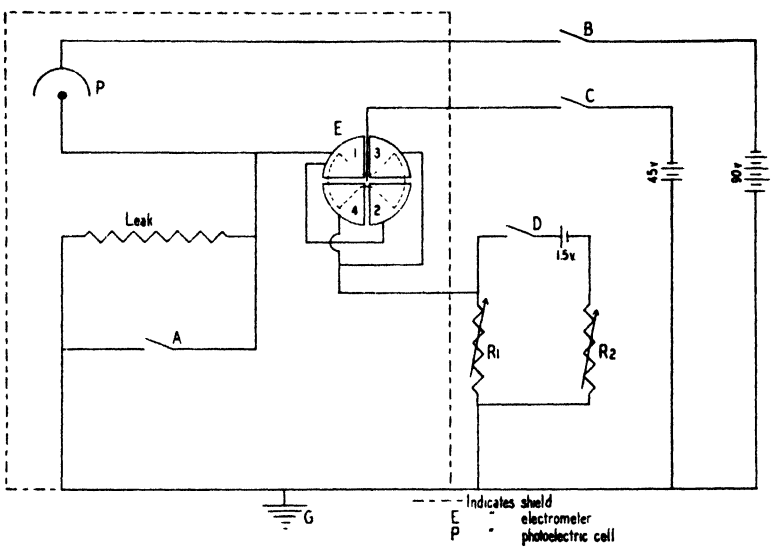

FIG. 2. ELECTRICAL CONNECTIONS

the current must flow through the high resistance leak to the ground and the quadrant pair 1–2 is charged, in accordance with Ohm's law, proportionally to the photoelectric current. The non-polarizable leak is a nearly saturated solution of iodine in benzene and has a resistance of 1.65×10^{11} ohms. Rollefson (2) gives specific resistances of such solutions. The solution was made of benzene, distilled from phosphorus pentoxide, and of triply sublimed iodine. It is sealed in a 5-mm. Pyrex tube with platinum wire contacts about 4 cm. apart. The whole is enclosed in a block of paraffin.

During light measurements, quadrants 3 and 4 are grounded through R_1. To calibrate the electrometer, switch D is closed, R_2 (10,000 ohms) is kept constant, and R_1 is varied. A plot is then made of quadrant poten-

tials against deflections, and is used to convert deflections to potentials existing across the leak.

The photoelectric cell used in the work here presented is the same cell whose wave length–sensitivity curve was described by Young and Pierce (3). It is quartz enclosed, has a cesium oxide surface, and is sensitive to both visible and ultraviolet light.

Within 4 mm. of slit 1, which is 1 cm. long, are two quartz absorption cells, 4 cm. in length and 2.4 cm. in diameter, with plane quartz windows. The cells, which are filled through tubes equipped with ground quartz stoppers, are mounted on a heavy metal carriage, adjustable in height and angle, by means of which either cell may be placed in the light beam. The moving part of the carriage and the ground switch A are controlled from the experimenter's position at the telescope through a pulley system. One cell contains pure solvent and the other the solution being studied. The solution cell is emptied through a stopcock connected to the quartz outlet with rubber tubing. The rubber is placed 5 cm. below the cell bottom, to prevent contamination of the solution in the illuminated portion. The solution cell may be emptied and refilled without being moved, at intervals determined by the solution's stability toward light. The light shield, with opening 16 mm. in diameter, between the condensing lens and the absorption cells confines the beam to the solution, preventing light reflection from the sides and edges of the cells. The light paths of different parts of the beam while passing through the solution are equal within 0.5 per cent.

From a measurement of I_0, the intensity of light passed through the solvent-filled cell of length x, and of I_x, the intensity of light passed through a similar solution-filled cell, the specific light absorption coefficient β may be calculated according to Lambert's law.

$$I_x = I_0 e^{-\beta x}$$

$$\beta = \frac{2.3 \log \frac{I_0}{I_x}}{x}$$

SENSITIVITY DATA

When it is desired to make many readings over a period of several days, as when the absorption spectrum is being investigated systematically at short intervals of wave length, the Dolezalek is a suitable electrometer. Its sensitivity is sufficient, remains constant for five or six days at a time (often for a period of a month or more), and is not subject to small temperature changes. The vane is charged at 45 volts because the corresponding sensitivity curve is a straight line for deflections up to 35 cm. Deflections of 0.74 to 1.25 mm. per millivolt are obtained. This sensitivity may

be varied somewhat by a change in the height of the vane. The vane is of aluminum, suspended by a quartz fiber, sputtered with gold.

For the much lower intensities encountered in the measurement of fluorescent light, the Compton electrometer yields good results. An aluminum vane, suspended by a Wollaston wire suspension 0.0003 cm. in diameter, is used. With the vane at a potential of 67.5 volts, the sensitivity in the useful range varies from 5.8 to 7.4 mm. per millivolt. The sensitivity may be regulated by the position of the vane or of the adjustable quadrant. The sensitivity curve deviates more from a straight line than does that of the Dolezalek, and the sensitivity varies appreciably from day to day and even from hour to hour, so that readings must be taken quickly or the sensitivity measured very often if results are to be accurate.

The "dark current," i.e., the current through the photocell when the shutter is closed, is reduced by a grounded pool of mercury placed in the depression of the photocell around the glass tubes that contain the tungsten conductors. The dark current is thus confined to the glass between the conductors and to the inner surface of the glass. It is somewhat variable, causing 1 to 10 mm. deflections of the Dolezalek electrometer and 8.5 cm. deflection of the Compton when the leak of 1.65×10^{11} ohms is used.

From the sensitivity of the Dolezalek electrometer and a measurement of the time required for a known small photoelectric current to cause a deflection of 24 cm., the *effective* capacity of the system was calculated. The value obtained was 1.33×10^{-3} microfarads (i.e., 120 cm.). This is larger than the true capacity, since some current passed through the leak to the ground during the measurement. The capacities of the Dolezalek and Compton electrometers are 80 cm. and 12 cm., respectively. When the Dolezalek is replaced by the Compton electrometer, the *effective* capacity of the system, including photocell anode, leak, and connections, is therefore about 50 cm. Capacity is a factor in the time of charging when such small currents are used.

Large changes in the sensitivity of either system may be produced by substitution of leaks of different resistances. This may be accomplished most easily by a variation of the iodine concentration. A second leak (L_2) was prepared from a solution of about 1 g. of iodine per 100 g. of solution. With L_2 and a Compton electrometer at a sensitivity of 7.4 mm. per millivolt, the dark current produces a deflection of about 100 cm. These deflections may be eliminated by a negative charge imparted to the quadrant pair 3–4 by a potentiometer circuit. From the potential required, the resistance of L_2 is estimated to be about 6×10^{12} ohms, i.e., about thirty-five times that of L_1.

CURRENT SENSITIVITIES

The maximum current sensitivities of the Compton, as used in this work (vane at 67.5 volts), are of the order of 8×10^{-16} amperes per millimeter

with L_1, and 2.2×10^{-17} amperes per millimeter with L_2. With the Dolezalek, these sensitivities are about one-sixth as great; one of 5×10^{-15} amperes per millimeter has often been used. With L_1, the time required for the vane to be deflected and come to rest is about one minute. With L_2, because of the smaller currents involved, this period is 10 minutes or longer, far too long when many readings are desired.

From the magnitudes of the current sensitivities, the resistances of L_1 and L_2, and the dark currents given above, the resistance of the photocell in the dark is estimated to be approximately 10^{15} ohms, about 10,000 times that of L_1 or 300 times that of L_2. This is about the order of magnitude expected for the resistance of Pyrex glass (4).

MONOCHROMATIC QUALITY OF LIGHT

A Zeiss fixed-arm spectroscope with deviation of 90° was converted into a monochromator by replacement of the eye-piece with a slit provided for the purpose. The lens (l_2) was clamped in a fixed position. The position of l_1 was then found for which the more brilliant mercury lines were in sharp focus at slit 2. When the lenses were so adjusted, the distances from the slits to the corresponding lenses were equal and the light was parallel when it passed through the prism. By use of the mercury arc, the prism was then fixed in such a position that the settings of the wave length scale were accurate to within one or two Ångström units.

The effectiveness of certain slit apertures was studied; the half-intensity widths, *H*, figure 3, of several mercury lines, were estimated from the intensity curves determined with the Dolezalek electrometer. By this method the widths of spectral regions, isolated by the monochromator with narrow slits, were found to vary from approximately 3 A.U. at λ4000 A.U. to 13 A.U. at λ7000 A.U. To investigate the ability of our system to isolate and measure narrow regions of the spectrum, the *D* doublet emitted by an Akatos sodium lamp was studied. The electrometer deflection curves are given in figure 4 for two experiments. The Compton electrometer was not available when this experiment was performed. If it were employed, narrower slits could probably be used and a precise comparison of the intensities of the two lines might be practical even with a small monochromator such as ours. With sufficient light intensity such as may be obtained from line spectra, and with greater resolving power, better separation can, of course, be obtained.

USES OF APPARATUS

Absorption spectra

The equipment has been used chiefly for obtaining specific light absorption coefficients of solutions, with a Dolezalek electrometer and the leak

of 1.65 × 10^{11} ohms resistance. The light source is a 900-watt T-20 Mazda C clear projection lamp, operating on a maximum of 30 volts. The voltage

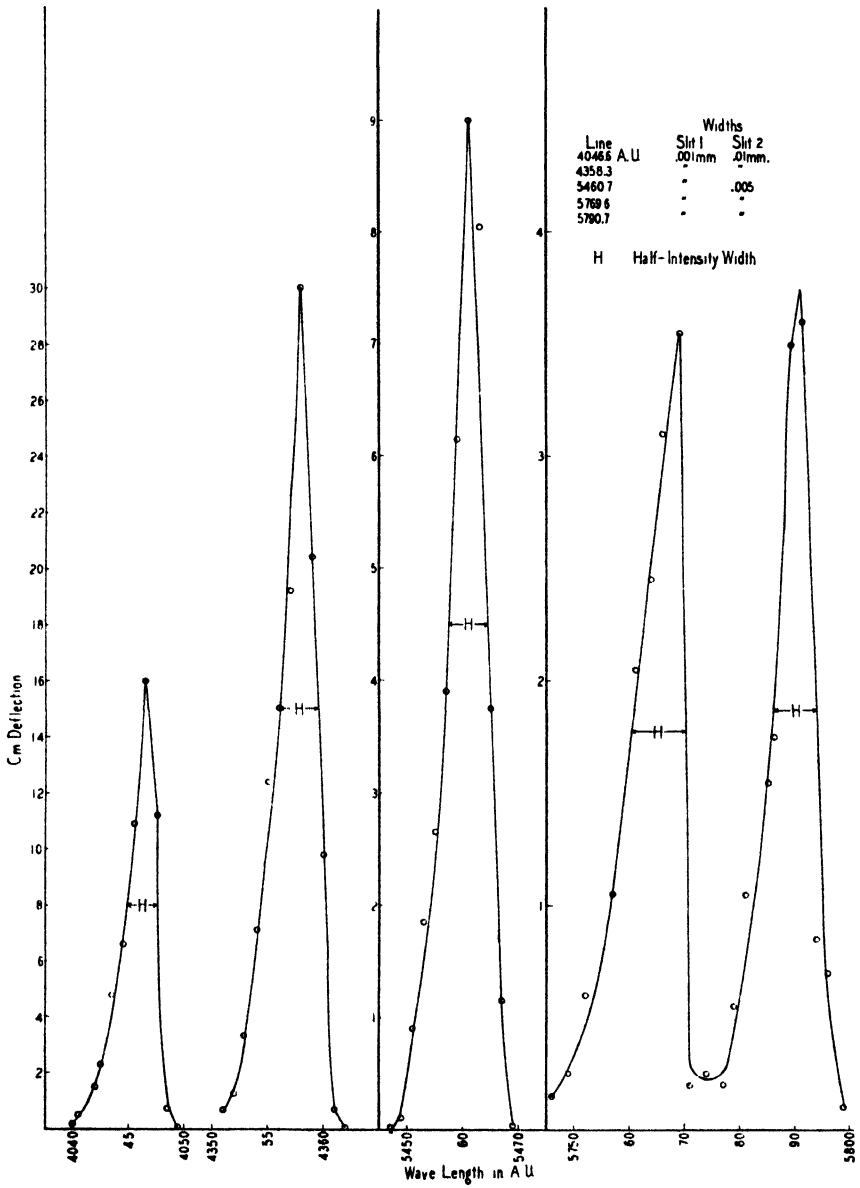

FIG. 3. LINES OF MERCURY ARC

is supplied by a direct current generator in parallel with a series of 6-volt radio "A" batteries, so arranged with resistance coils that the battery

voltage is slightly above the generator voltage delivered to the lamp. Only 0.1 to 1.0 ampere is drawn from the batteries and a current nearly free from fluctuations is delivered to the lamp. The lamp gives sufficient light in the visible when operating on 20 to 26 amperes. It is surrounded on four sides with shields, which decrease fluctuations in temperature caused by air currents.

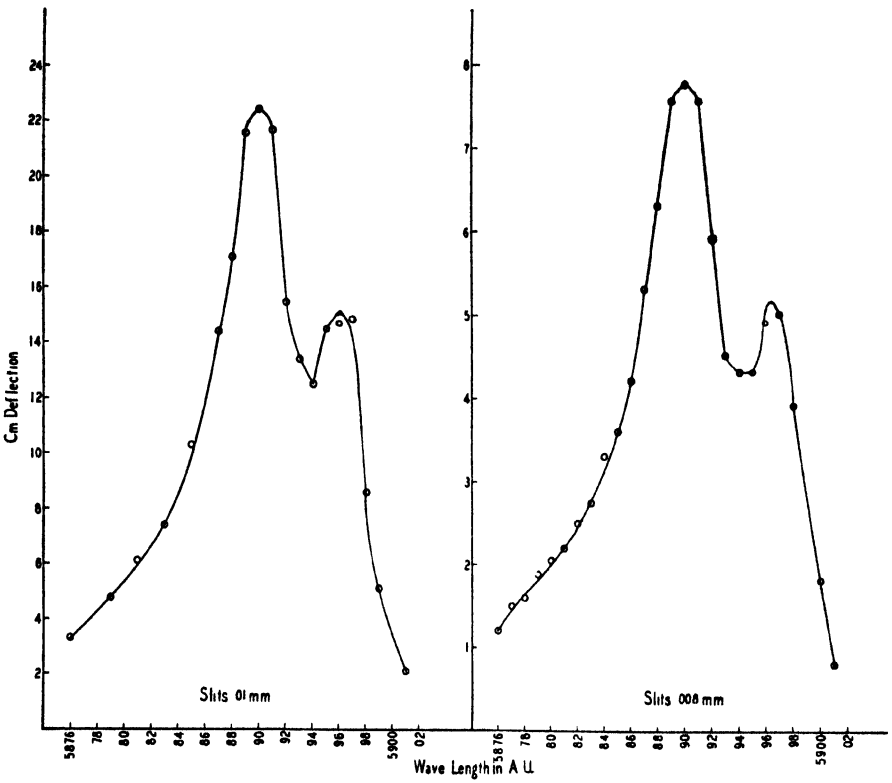

FIG. 4. SODIUM *D* LINES

To illustrate resolution with small monochromator

The slit widths are so chosen that I_0 produces a deflection of 20 to 35 cm. For the Mazda lamp, operating at 600 watts or less, they are approximately 0.001 mm. at λ7800 A.U., 0.002 mm. at λ6000–7000 A.U., 0.004 mm. at λ5000 A.U., 0.02 mm. at λ4000 A.U. and 0.03 mm. at λ3950 A.U. Such slit apertures make it possible to isolate regions varying in width from about 6 A.U. at λ4000 A.U. to 13 A.U. at λ7000 A.U. To isolate a spectral region 3 A.U. wide at λ4000 A.U. by the use of narrower slits, the current consumption of the lamp should be increased.

About three minutes are required for the three determinations necessary

for the calculation of one absorption coefficient. I_x is compared with the mean of two values of I_0, one taken before and one after I_x. Differences in I_0 reveal any accidental variations in light intensity.

The absorption cells, filled with solvent, should transmit as nearly as possible the same amount of light. There is no difficulty in placing them so that 30-cm. deflections agree within 3 mm., i.e., 1 per cent. With care they may be made to agree within 0.5 mm. After a series of many readings, during which the solution cell is emptied and refilled as many as ten times, the relative transmission of the cells containing solvent does not differ from the original value by more than 1 per cent. This small differ-

TABLE 1*

Absorption data for solution of chlorophyll

Source of light a Mazda lamp

WAVE LENGTH	SOLVENT FIRST DEFLECTION	SOLVENT SECOND DEFLECTION	MEAN SOLVENT DEFLECTION	SOLUTION DEFLECTION	I_0	I_x	$\frac{I_0}{I_x}$	LOG $\frac{I_0}{I_x}$
A U	*cm*	*cm*	*cm*	*cm*	*millivolts*	*millivolts*		
4300	25 10	25 05	25.07	13 50	337	184	1 831	0 2627
4300	25 05	25 00	25 02	13.50	337	184	1 831	0 2627
4300	24 50	24 45	24.47	13 20	329	180	1 828	0.2620
6600	24 65	24 60	24.62	15 00	331	204	1.622	0 2101
6600	24 60	24 35	24 47	14 90	329	203	1.621	0 2098
6600	24 35	24 60	24 47	14 95	329	203	1 621	0 2098

* Examples of absorption data from certain ether solutions of chlorophyll used in this laboratory. For each wave length, the data and calculations of three successive determinations of log I_0/I_x are given. The solvent deflections, taken before and after the solution deflections, are in columns 2 and 3, respectively. In column 4 is the mean of the solvent deflections. Column 5 contains the solution deflections. In columns 6 and 7 are the quadrant potentials (taken from the Dolezalek electrometer sensitivity curve) necessary to produce the deflections listed in columns 4 and 5, respectively. These potentials are directly proportional to the photoelectric current.

ence between the cells is thus relatively constant and affects but slightly the relative values of absorption coefficients.

Since the refractive indices of the solvent and dilute solutions are nearly equal, no appreciable change of the light focus on the slit is caused by an exchange of the absorption cells. For comparisons of some media having widely different refractive indices it may be necessary to take precautions to eliminate serious errors due to change of focus.

Magnitude of error

When conditions are steady and the lamp filament has reached a constant temperature (usually within fifteen minutes), the deflection caused by light

of any wave length may be reproduced after three minutes within the precision of reading, 0.5 mm. In routine spectral analysis most readings of I_0 check within 0.5 per cent; determinations are repeated when I_0 is not reproduced within 1 per cent. I_x is equally precise if the deflection is large enough.

With the electrometer working under good conditions, the zero point may be reproduced within 0.5 mm. after as many as twenty successive determinations of β, without a return of the vane to the zero position in the meantime.

If 0.5 per cent errors in I_0 and I_x both contribute to a 1 per cent error in I_0/I_x, the ratio may appear to be 2.02 when the true value is 2.00. The log of 2.02 is 0.3054, about 1.5 per cent larger than the log of 2.00 (0.3010). Since log I_0/I_x is proportional to the specific absorption coefficient θ (and the molecular absorption coefficient α, if Beer's law holds), the precision in this example is 1.5 per cent. Most of the values obtained are more precise than this. As deflections for I_x or I_0 decrease to small values, however, the error in log I_0/I_x increases.

Table 1 illustrates the reproducibility of results for a Mazda source.

Fluorescence spectra

This system is well adapted to the spectral measurement of fluorescent light from strongly fluorescent solutions, such as that of chlorophyll in ether. A tapering fluorescence tube is placed next to the slit, from which the guard window has been removed so that the point of origin of the fluorescent light may be as near the slit as possible. The exciting light from the 900-watt Mazda lamp enters the tube at right angles to the collimator through a plane window. About 1 mm. from this window and just in front of slit 1, it is brought to a focus.

With a Compton electrometer having a sensitivity of 6 mm. per millivolt, leak 1, and slits 0.03 mm. wide, maximum deflections of 25 cm. are produced by fluorescent light of λ6690 A.U. from ether solutions containing 0.015 g. of chlorophyll *a* per liter. Twenty-five seconds are required for each reading. Smooth curves were obtained for the fluorescence bands, whose maxima may be reproduced within 10 A.U. Successive deflections for the same wave length may be repeated within 0.5 per cent. To obtain the true fluorescence intensity–wave length curve, the sensitivity–wave length curve of the photocell must be determined and combined with these fluorescence data.

Data for chlorophylls *a* and *b*, obtained by use of this instrument, are to be reported soon by one of us (F. P. Z.).

SUMMARY

The photographic method is not satisfactory for measurement of opacity with a precision better than 5 per cent. In the usual photoelectric methods, comparatively wide spectral regions are employed. A photoelectric method of higher precision is available, which may be used for the measurement of relative intensities of light emitted from a continuous source, though limited to very narrow spectral ranges. A monochromator, photocell, electrometer, and high resistance leak are used. Photoelectric current sensitivities as great as 2×10^{-17} amperes per millimeter permit the use of slits so narrow that spectral regions varying in width from 3 A.U. at λ4000 A.U. to 13 A.U. at λ7000 A.U. may be investigated with a small standard monochromator, without amplification of the photoelectric current. A 900-watt Mazda lamp may be used for absorption spectra measurements.

Specific absorption coefficients and opacities may be determined with a precision better than 1.5 per cent and 1.0 per cent, respectively. Examples of data are presented. The method is well adapted to the spectral measurement of fluorescent light from strongly fluorescent solutions.

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THE ADSORPTION OF COPPER SULFATE BY SPHALERITE AND ITS RELATION TO FLOTATION

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In the recovery of sphalerite (ZnS) by the flotation process, the mineral must almost invariably be activated, i.e., a soluble heavy-metal salt (in practice, copper sulfate) must first be added before the mineral can be successfully floated. The problem of the activation of sphalerite by copper sulfate has been the object of a great deal of attention, and the general consensus of opinion is that the copper sulfate reacts with the zinc sulfide to form the more insoluble cupric sulfide at the surface of the sphalerite (1). Although Taggart (2) seems to consider the film to be cuprous sulfide, and Cox and Wark (3) are skeptical as to the completely chemical nature of the activation, the formation of a film of cupric sulfide appears to be the most probable explanation from the experimental evidence which exists.

If the formation of a film of cupric sulfide according to the reaction

$$ZnS + Cu^{++} = CuS + Zn^{++}$$

be accepted as a working hypothesis, the thickness of the film is a matter of considerable interest. In order to obtain information concerning this, a series of tests was made to determine the amounts of copper adsorbed by various sizes of sphalerite. The mineral was carefully sized and deslimed as described by Kidd and Wall (4).

Since cupric ion reacts with metallic iron, it was very essential to remove all traces of the latter (which might have been introduced into the mineral in the crushing and grinding processes) from the sphalerite. Most of the iron was removed by means of a strong electromagnet, the mineral being cleaned with the magnet both before and after grinding and before and after sizing. To remove the final traces, the sized and deslimed mineral was leached for eighteen hours with 6 normal hydrochloric acid, and then thoroughly washed with copper-free distilled water and allowed to dry. A 50-g. sample was weighed out and treated with 1 normal hydrochloric acid to remove any oxide film which might have formed during drying. The acid was washed out as before, and 250 cc. of 0.02 *M* copper sulfate was added. The solution was very carefully analyzed iodimetrically with

0.01 N thiosulfate before it had been added to the mineral and also after it had been in contact with the mineral for varying lengths of time. It was found, however, that practically all the adsorption took place during the first minute, there being no appreciable change in the concentration of the solution after that length of time. In column 4 of table 1 are given the amounts of copper adsorbed per gram of sphalerite for the various sizes studied.

Some of the results obtained by Kidd and Wall (4) are also of interest in this problem. Using 0.15 lb. of potassium ethyl xanthate and 0.15 lb. of cresylic acid per ton of sphalerite, they found that best flotation recoveries were obtained with 0.1 lb. of $CuSO_4 \cdot 5H_2O$ per ton of mineral for particles larger than 104 microns, with 0.2 lb. per ton for particles between 104 and 74 microns, and with 0.3 lb. per ton for particles finer

TABLE 1

PARTICLE SIZE	MILLIGRAMS OF COPPER PER GRAM OF ZINC SULFIDE FOR MONOMOLECULAR FILM	MILLIGRAMS OF COPPER PER GRAM OF ZINC SULFIDE FOR MAXIMUM RECOVERY	MILLIGRAMS OF COPPER PER GRAM OF ZINC SULFIDE ADSORBED IN ADSORPTION TESTS	"THICKNESS" OF FILM
microns				
−295+208	0 01012	0 0127	0 53	51 3
−208+147	0 01433	0 0127	0 60	41 8
−147+104	0 02033	0 0127	0 68	33 5
−104+74	0 02867	0 0254	0 76	26 5
−74+52	0 04050	0 0381	0 88	21 7
−52+37	0 05733	0 0381	1 00	17 5
−37+26	0 08099	0 0381	1 20	14 8
−26+18 5	0 1147	0 0381	1 40	12 2
−18 5+13	0 1620	0 0381	1 60	9 9
−13+9 2	0 2298	0 0381	1 80	7 8
−9 2+6 5	0 3250	0 0381	2 20	6.8

than 74 microns. With greater or smaller amounts than these, the recoveries decreased. These results, expressed as milligrams of copper per gram of sphalerite, are listed in column 3 of table 1.

In order to interpret the results of these two sets of experiments, it is first necessary to determine, for the various sizes, the amounts of copper required to form a monomolecular film on the surfaces of all the particles in one gram of sphalerite. This was done in the following manner, the −295+208 micron size being used as an example.

For this size range, the average particle size is 0.0252 cm. If it be assumed that the particles are in the form of regular tetrahedra (the ideal crystal form of sphalerite) having edges of this length, the volume of each particle is 1.886×10^{-6} cc. and the area is 1.10×10^{-3} sq. cm. (For regular tetrahedra, $V = 0.11785\ L^3$ and $A = 1.732\ L^2$, where L is the length of

the edge.) Since the density of sphalerite is 4.1, the volume occupied by 1 g. is 0.244 cc. Dividing this by the volume of one particle gives 1.293×10^5 as the number of particles per gram, which, multiplied by the surface area of one particle, gives 142.2 sq. cm. as the total surface area of 1 g. of the mineral.

The lattice constant for sphalerite is 5.43 A.U. (5) and the unit cell contains two zinc atoms in one surface. Consequently there is one zinc atom in a surface area of $\frac{1}{2}$ $(5.43 \times 10^{-8}$ cm.$)^2$, or 1.474×10^{-15} sq. cm. Dividing this into the total surface area of 1 g. of the sphalerite gives 9.647×10^{16} as the number of atoms of zinc present in the surface of 1 g. of the $-295+208$ micron sphalerite. If, in accordance with the reaction given above, it be assumed that each of these zinc atoms reacts with a copper ion, this will also be the number of copper ions required to form a monomolecular film, and is equivalent to 0.01012 mg. of copper per gram of sphalerite. The corresponding amounts of copper for all the sizes studied are given in column 2 of table 1.

DISCUSSION

A comparison of the second and third columns of table 1 shows that for particles larger than about 37 microns the amount of copper which gives the best flotation recovery is equal, within experimental error, to the amount required to form a monomolecular film. For smaller particles, however, maximum recoveries are obtained with considerably less copper than is required for a monomolecular film, and the difference increases rather rapidly with decrease in particle size. A probable explanation of these facts is that with the larger particles a practically complete monomolecular film is required in order to provide sufficiently strong attachment to the air bubbles to enable the particles to remain attached throughout the flotation process; the reason that a greater amount of copper decreases the recovery may be due to reaction between the excess copper and xanthate, decreasing the concentration of the latter below its optimum value. (Kidd and Wall (4) found that 0.15 lb. of potassium ethyl xanthate per ton of sphalerite gave the optimum recoveries with particles larger than about 37 microns; with either more or less xanthate the yields were decreased.) With the smaller particles it seems quite likely that strong enough attachment could result with less than a complete monomolecular film, and since the weight of a particle decreases more rapidly than its area, the fraction of the area which would have to be filmed with copper would decrease with decrease in size.

In column 5 of table 1 are given the "thicknesses" of the films of copper sulfide obtained in the adsorption experiments. These values were obtained by dividing the figures in the fourth column by the corresponding figures in the second, and are given purely for the purpose of comparison,

since nothing is known of the arrangement of the molecules in the adsorption layer. Two facts, however, are immediately evident: first, the films formed on sphalerite in a solution of the strength used (many times that used in flotation practice) are apparently many molecules thick, and second, this "thickness" decreases as the particle size decreases. When the logarithm of the "thickness" is plotted against the logarithm of the average particle size, a straight line (figure 1) is obtained, which, when extrap-

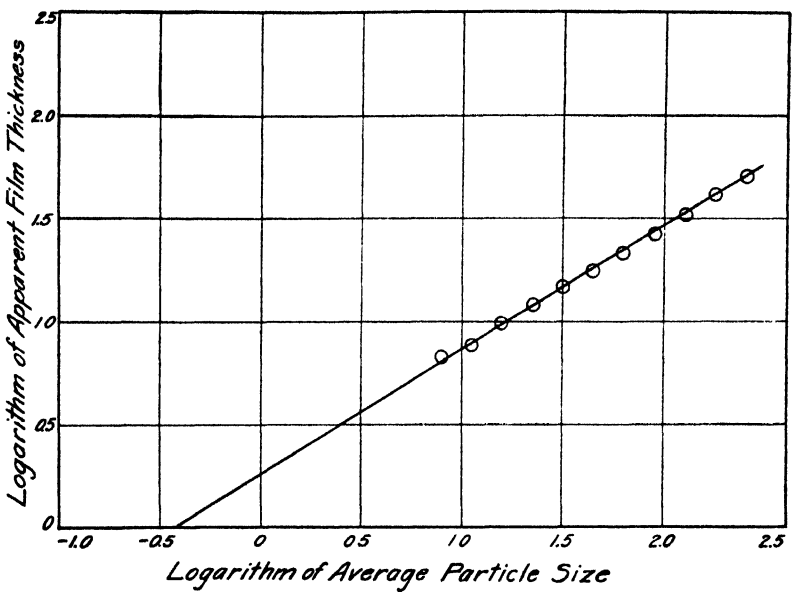

FIG. 1. VARIATION OF APPARENT THICKNESS OF ADSORBED FILM WITH SIZE (IN MICRONS) OF SPHALERITE PARTICLES

olated, indicates that a monomolecular film would result with particles 0.37 micron in size. The equation

$$T = \left(\frac{d}{0.37}\right)^{0.608}$$

where T is the apparent film thickness and d the particle size in microns, fits the curve very well.

These facts are difficult to explain on the basis of familiar concepts. A possible explanation may lie in the change of surface forces with size; as the size decreases the initially formed layers of copper sulfide may become more compact, thus rendering diffusion more difficult, which would tend to decrease the thickness of the films. It is rather difficult, however, to conceive of any change in surface forces becoming appreciable in the larger sizes studied.

The recent theory of the mosaic or block structure of crystals leads to a more probable explanation. This theory, developed theoretically by Zwicky (6) and supported by the excellent experimental work of Goetz (7) on single bismuth crystals, states that all crystals have, besides their regular crystal structure, a much larger secondary structure manifested by periodic changes in density. Goetz found the resulting "blocks" to be approximately 1.4 microns in length. The work of Dean, Gross, Brighton, and St. Clair (8) indicates that in the case of galena the blocks have a length of less than 20 microns, and they consider it possible for certain molecules (e.g., H_2S) to penetrate between these blocks.

The results of the adsorption experiments can be explained by assuming that the copper ions penetrate to a certain extent between the elementary blocks of the sphalerite crystals, as well as forming a monomolecular film on the surfaces. When the individual blocks are liberated, only the amount of copper required to form a monomolecular film will be adsorbed, and from figure 1 it appears that for sphalerite the size of these blocks is 0.37 micron. It is obvious that the larger the particles, the more crevasses between blocks there will be for copper ions to diffuse into, and accordingly, the greater will be the apparent film thickness. This explanation does not necessarily conflict with that offered for the results of the flotation experiments. In the latter, the solutions were very dilute in copper and the total amount present was never appreciably greater than the amount required for a monomolecular film. It seems quite reasonable to suppose that the copper ions would react with zinc atoms in the surfaces exposed in preference to penetrating between the blocks.

SUMMARY

1. With sphalerite particles larger than about 37 microns, the amount of copper sulfate which gives the best flotation recoveries is equal to the amount required to form a monomolecular film of cupric sulfide.

2. With smaller particles, maximum recovery is obtained with less than the amount of copper sulfate required for a monomolecular film, the difference between the amount required for maximum recovery and that required for a monomolecular film increasing with decrease in particle size.

3. A simple explanation is offered to account for these flotation results.

4. The amounts of copper adsorbed by sphalerite of various sizes from a 0.02 *M* copper sulfate solution are equivalent to surface films of copper sulfide many molecules thick. These "thicknesses," however, decrease as the particles become smaller.

5. An explanation of the results of the adsorption tests by change of surface forces with size appears improbable. The theory of the mosaic structure of crystals, however, provides an explanation which agrees very satisfactorily with the results obtained.

6. The adsorption tests indicate that the unit blocks of sphalerite are approximately 0.37 micron in length.

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A NEW THEORY OF FERRIC OXIDE HYDROSOLS

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INTRODUCTION

Among the contributions to the chemistry of so-called iron oxy hydrosols, three originated in this laboratory. Thomas and Frieden (1), studying iron oxychloride sols, reported a constant ratio of iron to chloride when sols were dialyzed to incipient precipitation, and they offered the solution link theory to explain the nature of sol stability, according to which the micellar agglomerate was kept in solution by the solution forces inherent to the ferric chloride associated with the other constituents forming the micelle. Hamburger (2) prepared iron oxybromide sols and reported no constant ratio of iron to anion (purity) although, on the whole, the bromide sols appeared to be more stable than the chloride sols studied simultaneously. Mabee (3) prepared and studied the properties of ferric oxyacetate hydrosols. He found a constant purity and, in general, lower stability than was reported for the two types of sols previously studied. Both Hamburger and Mabee believed their results to be in harmony with an hydrolytic definition of hydrosols, and with the above mentioned solution link theory.

It was thought that a study of ferric oxypropionate sols might be an interesting comparison with these sols investigated earlier.

PRELIMINARY EXPERIMENTS

Ferric hydroxide was made by electrolysis of water, to which was added a few drops of sodium hydroxide solution to provide conductivity, using an iron anode and a carbon cathode. The ferrous hydroxide thus formed was oxidized by air, and the resulting ferric hydroxide was washed by decantation.

Attempts to peptize this product with propionic acid seemed unsuccessful, and this method of sol preparation was discarded. It was thought that the precipitate was too granular and too little hydrated to be readily peptized. Next, some pure iron filings were dissolved in dilute propionic acid; after standing several days, during which time there was a very slow evolution of hydrogen, a sample of the ferrous propionate solution was oxidized

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by treatment with hydrogen peroxide to absence of ferrous iron test with ferricyanide. (If the solution were not completely oxidized, it was found that addition of ammonium hydroxide yielded a black precipitate, which, upon drying, proved to be magnetic.)

The ferric propionate solution was then put into collodion membranes for dialysis to incipience of precipitation. In a very short time, small amounts of reddish-brown flocculate had appeared, so four different sols were immediately analyzed, without contrifuging out the excess precipitated iron. The respective purities $\frac{\text{(equiv. Fe)}}{\text{(equiv. Anion)}}$ were found to be 1.2, 4.3, 3.8, and 1.1, while still another sample, intentionally somewhat beyond incipience of precipitation, was found to have a purity of only 5.1.

In these analyses, the iron was determined (4) by heating to white fumes with sulfuric acid, passing through a Jones' reductor, and titrating with standardized permanganate solution. The propionate was determined (5) by heating, hydrolyzing, salting out, and titrating with standard sodium hydroxide solution, using phenolphthalein as an indicator.

The fact that these iron propionate solutions should contain such a relatively small amount of iron in proportion to anion, as compared to sols previously studied, was entirely unexpected, and led to consideration of the possibilities suggested in the following section.

THEORETICAL

Besides the investigators already mentioned, several other colloid chemists have expressed beliefs that colloidal iron solutions underwent hydrolytic changes. Among these are Malfitano (6), Buzágh (7), Pauli and Matula (8), Tian (9), and others, but none of them has suggested any theoretical treatment or procedure to enlarge such beliefs. Therefore, the following development has been made, while fully realizing that in such complex systems as are dealt with, the considerations of equilibria must of necessity be rather loosely construed; this method of treatment is thus offered and utilized as a means to arrive at some interesting relations.

Keeping this in mind, we may say at once that if colloidal solutions are formed by progressive hydrolysis, they should follow laws analogous to those derived for the hydrolytic relations from the law of mass action. According to these derivations, a salt of the type MA_3 may have two possibilities in hydrolyzing, the distinction being based upon whether the acid formed is weakly or highly dissociated. First considering the strong acid type, from the equation

$$MA_3 + 3H_2O \rightleftharpoons M(OH)_3 + 3HA$$

letting x represent the amount hydrolyzed, and v the volume in liters containing one mole of salt, and assuming both salt and acid to be completely ionized, we have

$$k = \frac{[M(OH)_3]\,[HA]^3}{[MA_3]\,[H_2O]^3}$$

Since the $[H_2O]$ is constant in aqueous solution

$$K_{hyd.} = \frac{[M(OH)_3]\,[HA]^3}{[MA_3]} = \frac{\left[\frac{x}{v}\right]\left[\frac{3x}{v}\right]^3}{\frac{1-x}{v}} = \frac{27\,x^4}{(1-x)\,v^3} \tag{1}$$

Since

$$[H^+]\cdot[OH^-] = s_{H_2O}$$

then

$$[H^+] = 3x = \frac{s_{H_2O}}{[OH^-]}$$

so

$$[OH^-] = \sqrt[3]{K_{M(OH)_3}\,\frac{[M(OH)_3]}{[M^{+++}]}}$$

and since

$$[M^{+++}] = \frac{1-x}{v}$$

then

$$[OH^-]^3 = K_{M(OH)_3}\,\frac{[M(OH)_3]}{\frac{1-x}{v}}$$

Moreover

$$[\text{Total acid}]^3 = \frac{s^3_{H_2O}}{K_{M(OH)_3}\,\frac{[M(OH)_3]}{\frac{1-x}{v}}}$$

Therefore

$$K_{hyd.} = \frac{27\,x^4}{(1-x)\,v^3} = \frac{[M(OH)_3]\left[\frac{s^3_{H_2O}}{[K_{M(OH)_3}]\,\frac{[M(OH)_3]}{\frac{1-x}{v}}}\right]}{\frac{1-x}{v}} = \frac{s^3_{H_2O}}{K_{M(OH)_3}}$$

But when the acid formed by the hydrolysis is little ionized:

$$[M(OH)_3] = \frac{x}{v},\ [OH^-] = \sqrt[3]{K_{M(OH)_3}\frac{[M(OH)_3]}{[M^{+++}]}},\ [M^{+++}] = \frac{1-x}{v},\ \text{and}$$

$$[A^-] = \frac{3(1-x)}{v}$$

$$[OH^-] = \frac{s_{H_2O}}{[H^+]} = \frac{s_{H_2O}}{K_{HA}\frac{[HA]}{[A^-]}}$$

$$K_{M(OH)_3}\frac{[M(OH)_3]}{[M^{+++}]} = \frac{s^3_{H_2O}\,[A^-]^3}{K^3_{HA}\,[HA]^3}$$

$$K_{hyd.} = \frac{s^3_{H_2O}}{K^3_{HA}\cdot K_{M(OH)_3}} = \frac{[M(OH)_3]\,[HA]^3}{[M^{+++}]\,[A^-]^3} = \frac{\left(\frac{x}{v}\right)\left(\frac{3x}{v}\right)^3}{\left(\frac{1-x}{v}\right)\left(3\left(\frac{1-x}{v}\right)\right)^3} = \frac{x^4}{(1-x)^4}$$

$$K_{hyd.} = \frac{x^4}{(1-x)^4} = \frac{s^3_{H_2O}}{K^3_{HA}\cdot K_{M(OH)_3}} \qquad (3)$$

Therefore in the latter type of hydrolysis the reaction is independent of dilution, whereas in the first type the extent of the hydrolysis varies as $\sqrt[4]{v^3}$.

Now in the case of colloidal solutions, if we consider the complex as a somewhat soluble but little ionized *base*, ionized into Fe^{+++} and OH^- ions, we have exactly the same conditions if the so-called chemical (hydrolytic) point of view of hydrosols is correct,—up to the point of incipience of precipitation when the relations expressed above break down, and undergo a complete change due to the formation of insoluble bases. But from the point of true (ionic) solution through colloidal (micelle) formation to the beginning of precipitation, there is no apparent reason why colloidal iron solutions should not follow some such laws as those derived above, provided the solutions themselves are undergoing purely chemical reactions. This state of affairs might be expressed by some such system as

$$\begin{array}{l}(Fe(OH)_3)_M\cdot(x)Fe^{+++} + 3(x)\ A^- \\ \quad\downharpoonleft\!\!\uparrow \\ (Fe^{+++}) + 3(OH^-)\end{array}$$

This might be progressively hydrolyzed to

$$\begin{array}{l}(Fe(OH)_3)_N\cdot(y)Fe^{+++} + 3(y)A^- + (x-y)HA \\ \quad\downharpoonleft\!\!\uparrow \\ (Fe^{+++}) + 3(OH^-)\ \text{ where }\ x > y\ \text{ and }\ N > M\end{array}$$

For a sol of purity = 20, the hydrolytic "equation" might be written

$$20FeA_3 + 57H_2O \rightleftharpoons (Fe(OH)_3)_{19}\cdot FeA_3 + 57HA$$

As the acid formed is dialyzed away, the sol would analyze to 60 equivalents of iron and 3 equivalents of anion, thereby giving a purity of 20. If dialysis were continued, successive stages of hydrolysis would be reached, more $Fe(OH)_3$, less (Fe^{+++}) and (A^-) present, and hence higher purities. Then for the progressive hydrolysis of iron salts to colloidal solutions we have the two types of reactions, and the respective "colloidal hydrolysis constants:"

$$K_{\text{coll hyd}} = \frac{s^3_{H_2O}}{k_b} = \frac{27x^4}{(1 - x)\, v^3} \tag{4}$$

and

$$K_{\text{coll hyd}} = \frac{s^3_{H_2O}}{K_a^3 \cdot K_b} = \frac{x^4}{(1 - x)^4} \tag{5}$$

where K_a is the dissociation constant of the acid formed, and K_b represents the dissociation constant of the complex colloidal radical *as a base.*

Then the colloidal solutions of ferric chloride, bromide, nitrate, etc. should follow equation 4, while those of the acetate, propionate, and butyrate should follow equation 5.

Now although we do not know the respective K_b values of various iron colloids, at least we may safely assume that they are very small, and of the same order of magnitude.

Then if we consider the two salts $Fe(A_1)_3$ and $Fe(A_2)_3$, both of which form weak acids upon hydrolysis, we may write as the relation between their respective "colloidal hydrolysis constants:"

$$\frac{K_1}{K_2} = \frac{\dfrac{s^3_{H_2O}}{K^3_{HA_1} \cdot K_{b_1}}}{\dfrac{s^3_{H_2O}}{K^3_{HA_2} \cdot K_{b_2}}} = \frac{K^3_{HA_2}}{K^3_{HA_1}} \tag{6}$$

Then we see that the ratio of the "constants" is inversely proportional to the cubes of the dissociation constants of the respective acids produced by the hydrolysis, after having assumed that K_{b_1} and K_{b_2} are nearly equal.

If we call R this ratio,

$$\frac{K_1}{K_2} = \frac{K^3_{HA_2}}{K^3_{HA_1}} = R$$

then it is also true that

$$R = \frac{\dfrac{x_2^4}{(1 - x_2)^4}}{\dfrac{x_1^4}{(1 - x_1)^4}} \tag{7}$$

from which

$$\frac{x_2}{1 - x_2} = \sqrt[4]{R} \cdot \frac{x_1}{1 - x_1} \tag{7a}$$

or, in other words, the fraction of one salt hydrolyzed will always be a constant times the fraction hydrolyzed of the other salt (under the same conditions of time and temperature).

Dividing both sides of equation 7 by x_1^4, and multiplying both sides by x_2^4, we arrive at

$$\frac{\left(\frac{1}{1 - x_1}\right)^4}{\left(\frac{1}{1 - x_2}\right)^4} = \frac{x_2^4}{x_1^4} \cdot R$$

therefore

$$\frac{\frac{1}{1 - x_1}}{\frac{1}{1 - x_2}} = \frac{x_2}{x_1} \sqrt[4]{R}$$

Now as soon as appreciable purities are reached —high ratios of iron over anion—x_1 and x_2 become very nearly equal, and $\frac{1}{1 - x}$ is equal to the purity at incipience of precipitation as previously defined, therefore, approximately,

$$\frac{P_1}{P_2} = \sqrt[4]{R} \tag{8}$$

But for weak acids, R is quite small—for acetic and propionic it is only 2.4—so we may conclude that very nearly equal purities at incipience of precipitation should be found for two iron salts both of which yield weak acids upon hydrolyzing.

Another interesting application when a weak acid is formed is seen in the equalities set down below:

$$[H^+] = K_{HA} \frac{[HA]}{[A^-]} = K_a \frac{x}{1 - x} = K_a \times \sqrt[4]{\frac{s^3_{H_2O}}{K_a^3 \cdot K_b}} \tag{9}$$

or,

$$[H^+] = \text{a constant} \tag{10}$$

Also, it is interesting to point out that from equation 9 one may find the magnitude of K_b, if the pH is first determined.

Such calculations cannot be applied to sols where a strong acid is formed; first, because the changing dilution during dialysis must change the purity relationships, and secondly because the acid is dialyzed away, and there is no constancy possible here as was the case with the acetate.

Now again turning to the strong acids, it is evident, since the extent of the hydrolysis varies as $\sqrt[4]{v^3}$, that constant optimum purity values can be obtained only if no dilution takes place during dialysis. In other words, the purities of this type of sol at incipient precipitation should *not* be constant.

Neidle (10) reports this qualitatively for the oxychloride; Hamburger (2) for the ferric oxybromide sol. Thomas and Frieden report a constant purity for ferric oxychloride sol, but this may be due to the fact that the determinations were made on a sol of low concentration, which was divided into samples of various dilutions, after first undergoing the same preliminary dialysis, both of which procedures would help in masking differences in the sols at the end of the experiments.

It has been known for a long time that sulfate ion was a good precipitation or flocculation agent for iron oxysols. The theoretical derivations demand this, as may be seen from the following relationships:

$$Fe_2(SO_4)_3 + 6H_2O \rightleftharpoons 2\,Fe(OH)_3 + 3H_2SO_4$$

Using the same notations,

$$K = \frac{[Fe(OH)_3]^2\,[H_2SO_4]^3}{[Fe_2(SO_4)_3]} = \frac{\left(\frac{2x}{v}\right)^2\left(\frac{3x}{v}\right)^3}{\frac{1-x}{v}} = \frac{108\,x^5}{(1-x)\,v^4}$$

also

$$[H^+] = \frac{s_{H_2O}}{[OH^-]}$$

$$[\text{Total acid}] = \tfrac{1}{2}\,[H^+],$$

and

$$[OH^-] = \sqrt[3]{K_{Fe(OH)_3}\,\frac{[Fe(OH)_3]}{[Fe^{+++}]}}$$

then

$$[\text{Total acid}]^3 = \tfrac{1}{8}\left(\frac{s^3_{H_2O}}{[OH^-]^3}\right) = \tfrac{1}{8}\,\frac{s^3_{H_2O}}{K_{Fe(OH)_3}\,\frac{[Fe(OH)_3]}{[Fe^{+++}]}}$$

$$K = [Fe(OH)_3]^2 \cdot \tfrac{1}{8}\,\frac{s^3_{H_2O}}{K_{Fe(OH)_3}\,\frac{[Fe(OH)_3]}{[Fe^{+++}]}} \div [Fe_2(SO_4)_3] = \frac{\left(\frac{2x}{v}\right)^2\,\frac{s^3_{H_2O}\cdot 2\left(\frac{1-x}{v}\right)}{8K_{Fe(OH)_3}\cdot 2\left(\frac{x}{v}\right)}}{\frac{1-x}{v}}$$

$$= \frac{s^3_{H_2O}\cdot x}{2K_{Fe(OH)_3}\cdot v} = \frac{108\,x^5}{(1-x)\,v^4} \qquad (11)$$

from which it is evident, comparing equation 11 with equation 4, that K for ferric sulfate must be smaller than in the case of the chlorides, etc., for x is always less than 1 (in the case of the sulfate, indeed, it is probably very small) and V is always greater than 1, as fairly dilute solutions must be used if colloidal solutions are to be formed. In addition we have the factor 2 appearing in the denominator, which would make the sulfate even less "colloidal" compared with the other strong acid types.

The micelle as pictured according to the above relationships agrees very closely with the "solution link" theory of colloidal stability, the ferric hydroxide formed by the hydrolysis being dragged into solution by a soluble ferric salt which has previously been called the peptizing agent. As hydrolysis proceeds, the $Fe(OH)_3$ chain gets larger and larger until finally there is not enough of the peptizing agent present, and precipitation occurs. It should be noted that the law of mass action as used above has always been applied to the ("solution link") salt—not to the dispersed phase.

If the views here presented are the correct explanation of iron hydrosol stability, it would be natural to expect that flocculation should occur in a manner similar to ordinary precipitation, owing to the formation of insoluble compounds. Opponents of the chemical theory of hydrosol behavior have long used the known facts of different amounts of anions (sulfates, for instance), for sol precipitation in apparently no chemical or equivalent relationships, in their arguments. Nevertheless, it is possible that flocculation may be due to the formation of insoluble compounds which precipitate when a certain relationship similar to a solubility product constant is exceeded, and a theory is presented below in an endeavor to reconcile the conflicting views and evidence in this interesting matter.

As was pointed out above, the iron salt upon hydrolyzing acquires a longer and longer $Fe(OH)_3$ tail, or chain, the sol becoming more unstable as the purity rises. Then, coinciding with this progressive hydrolysis, it is not too far-fetched to expect successively lower "solubility product constants" (called below ion product constant) with successive hydrolytic stages (i.e., as N in $(Fe(OH)_3)_N \cdot FeA_3$ increases). According to this hypothesis the amount of sulfate necessary for precipitation should *decrease* with rising purity, which corresponds to lower Fe^{+++} ion concentration, as opposed to the analogous inorganic (ionic) solutions where a higher anion concentration is required if the cation concentration is lowered to satisfy a $K_{s.p.}$ As pointed out above, the reason for this anomaly is that as the purity increases the ferric ion concentration decreases, but as the constant governing the precipitation is also becoming successively smaller to govern the new conditions of the next stage of hydrolysis, then the sulfate ion concentration necessary for precipitation also decreases.

However, if there be any such governing factor analogous to a $K_{s.p.}$, it is evident that the ratio of ferric ions to sulfate ions in moles per liter should

remain constant throughout the range of purity changes. In table 1 are calculations from the data of Hamburger's dissertation (p. 20).

In table 1, Fe/Cl, or purity, and SO_4^{--} (in millimoles) are reported. $[Fe^{+++}]$ in millimoles per liter has been calculated from

$$\frac{\text{Total Fe (in milliequivalents)}}{3} = \text{Anion}$$

and

$$\frac{\text{Anion}}{3} = Fe^{+++} \text{ (in millimoles)}$$

Thus, the ratio SO_4^{--}/Fe^{+++} was computed. Similar calculations are given in the tables that follow. (The error in measuring the precipitation or "liminal" values, defined as the average between the amount just floccu-

TABLE 1*

Precipitation values for a chloride sol

Iron per liter = 415 milliequivalents

Fe/Cl or P	$[Fe^{+++}]$	$[SO_4^{--}]$	RATIO $[SO_4^{--}]/[Fe^{+++}]$
	millimoles per liter	*millimoles per liter*	
20	7	5 05	0 72
23	6	3 94	0 65
24	5 7	3 94	0 69
25 7	5 4	3 49	0 65
30 3	4 6	2 69	0 58
			Average = 0 66

* Calculations from the data of Hamburger's dissertation (see reference 2).

lating, and that failing to precipitate, is about ± 5 per cent.) Table 1 showed the precipitation values for a chloride sol; in table 2 are the values for a bromide sol.

Thus we see that these ratios are in harmony with the known facts concerning the relative stabilities of the two halides as "solution links." In other words, ferric oxy(bromide) sulfate is more soluble than ferric oxy(chloride) sulfate, at the same purity.

From Mabee's dissertation (pp. 31, 34, and 35) we can use data for the ferric acetate sols he studied, and make similar calculations (see table 3). Thus, ferric oxy(acetic) sulfate is less soluble than the other two considered above, which is in complete harmony with the known facts about these sols.

Using the above values for the respective ratios $[SO_4^{--}]/[Fe^{+++}]$, we can readily calculate from Hamburger's sulfate ion values, initially and at

precipitation (for this the values were taken from the dotted line indicating incipience of precipitation in the tables), the purity of the sols at these two stages of aging. (The data used in table 4 are taken from his tables VII to XII, pp. 24–6); from the average ratio value as found above, and the reported $[SO_4^{--}]$ value, Fe^{+++} can be calculated. The total iron in milliequivalents divided by this $[Fe^{+++}]$ gives the purity.

TABLE 2

Precipitation values for a bromide sol

Iron per liter = 415 milliequivalents

Fe/Br	$[Fe^{+++}]$	$[SO_4^{--}]$	RATIO $[SO_4^{--}]/[Fe^{+++}]$
	millimoles per liter	*millimoles per liter*	
20 4	6 7	7.47	1.11
22.2	6 2	7.15	1.15
25 6	5 4	6.12	1.13
25 7	5.37	5.96	1 10
29.8	4 6	5 00	1.09
33 5	4.1	4 24	1.03
38.5	3.6	3.65	1.01
41 8	3.3	3 62	1.10
			Average = 1 09

TABLE 3

Precipitation values for an acetate sol

Fe PER LITER	Fe/Ac	$[Fe^{+++}]$	$[SO_4^{--}]$	RATIO $[SO_4^{--}]/[Fe^{+++}]$
		millimoles per liter	*millimoles per liter*	
567	12	15 7	1.7	0.108
358	12.8	9.3	0.95	0.102
555	13	14 2	2.0	0.140
567	20*	9.4	1.0†	0.106
358	20*	5.9	0.5†	0.084
555	20*	9.3	1.0†	0.107
				Average = 0.108

* The value given by Mabee for purity at incipient precipitation.

† Values read off aging data at description of "brown, turbid," indicating incipient precipitation.

In some instances above, the precipitation purity is less than the starting purity. This discrepancy may be due to the fact that the difference between the initial and precipitation SO_4^{--} values is less than the 5 per cent error in determining these values. Similarly the allowable differences between calculated P and analytically determined P at the start is also at least ± 5 per cent.

Since the calculated initial P agrees fairly well with P by analysis, it seems that this calculation should apply equally well to P at incipient precipitation, and thus it will be noted in the above table that the purity upon aging to incipient precipitation is *not* constant for either bromide or chloride sols, which is in accordance with the predictions based upon hydrolytic considerations given in the derivations above. The reason for these P's being so low compared with previously reported values is that these solutions are much more concentrated than those dialyzed to precipitation.

Returning now to the idea of a "$K_{s.p.}$," if we consider the micelle as $(Fe(OH)_3)_N \cdot FeA_3$ to present an exceedingly simplified picture, then for a

TABLE 4

SOL	TABLE	TOTAL IRON	INITIAL SULFATE	INITIAL			PRECIPITATION SO_4^{--}	CALCULATED Fe^{+++}	PRECIPITATION (CALCULATED) P
				Calculated Fe^{+++}	Calculated P	Analytical P			
		milliequiv. per liter	*millimoles per liter*						
Br	VII	415	7 74	21	19 8	20 4	6 68	18 3	22 6
Cl	VIII	415	5 05	23	18 0	20 0	4 66	21 0	19 8
Br	IX	415	5 96	16 2	25 6	25 5	(6 20)*	16 8	24 5
Cl	X	412	3 50	15 9	25 9	25 7	(3 40)*	15 3	26 9
Br	XI	415	4 24	11 6	35 7	33 5	4 67	12 7	32 7
Br	XII	402	3 26	9 0	44 7	40 3	(3 67)*	10 0	40 3

* Interpolated at dotted line.

"solubility product" at any particular hydrolytic stage, we could write (for the sulfate)

$$\text{"}K_{s.p.}\text{"} = [(Fe(OH)_3)_N Fe^{+++}]^2 [SO_4^{--}]^3$$

or merely,

$$= [Fe^{+++}]^2 [SO_4^{--}]^3$$

$[Fe^{+++}]$ being calculated from $\frac{(\text{total Fe})}{P}$; but it was thought best in developing the analogy to refrain from calling this constant a "$K_{s.p.}$," since it cannot definitely be stated what solid phase is in equilibrium with the constant. It was therefore decided to name this constant an "ion product constant:"

$[Fe^{+++}]^2 [SO_4^{--}]^3 = K_{i.p.}$ (a factor governing the conditions existing in a sol at the determination of its sulfate liminal value.)

For the different stages in the acetate sols tabled above, this would give:—

(1) $K_{i.p.} = (15.7 \times 10^{-3})^2 (1.7 \times 10^{-3})^3 = 1.2 \times 10^{-12}$

(2) $K_{i.p.} = (9.3 \times 10^{-3})^2 (0.95 \times 10^{-3})^3 = 7.4 \times 10^{-14}$

(3) $K_{i.p.} = (14.2 \times 10^{-3})^2 (2 \times 10^{-3})^3 = 1\ 6 \times 10^{-12}$

(4) $K_{i.p.}$ = Same as (6)

(5) $K_{i.p} = (6 \times 10^{-3})^2 (0.5 \times 10^{-3})^3 = 4.5 \times 10^{-15}$

(6) $K_{i\ p.} = (9.3 \times 10^{-3})^2 (1 \times 10^{-3}) = 8.6 \times 10^{-14}$

It appears by inspection that the respective successive $K_{i.p.}$'s progress exponentially, with increase in P. If there is such an exponential progres-

TABLE 5

FOR THE ACETATE SOLS	FOR THE CHLORIDE SOLS (FROM TABLE 1)		FOR THE BROMIDE SOLS (FROM TABLE 2)	
	$K_{i.p}$	$\sqrt[P]{K_{i.p.}}$	$K_{i\ p}$	$\sqrt[P]{K_{i\ p}}$
(1) 0 1015	(1) 6×10^{-12}	0 27	(1) $1\ 8 \times 10^{-11}$	0.29
(2) 0 095	(2) 2×10^{-12}	0 31	(2) $4\ 4 \times 10^{-12}$	0 33
(3) 0.0102	(3) $1\ 8 \times 10^{-12}$	0 32	(3) $6\ 6 \times 10^{-12}$	0.37
(4) 0.222	(4) $1\ 2 \times 10^{-12}$	0.35	(4) $2\ 6 \times 10^{-12}$	0 41
(5) 0 191	(5) 4×10^{-13}	0 39	(5) $1\ 2 \times 10^{-12}$	0.47
(6) 0.222			(6) $6\ 6 \times 10^{-13}$	0.48
			(7) 5×10^{-13}	0.5
1 to 2×10^{-1}		3 to 4×10^{-1}		3 to 5×10^{-1}

sion, then if P is the purity, the Pth root of the $K_{i\ p}$ at that purity should give the $K_{i\ p.}$ of ferric oxy(halide) sulfate when x is exceedingly small. From which it is immediately apparent that if we take the root (of different $K_{i.p.}$'s) corresponding to the purities, we should obtain the same value.

In table 5 are shown these values, found by taking the Pth root of the $K_{i.p.}$'s as calculated above.

Thus we see that all give a value of the same order of magnitude, 10^{-1}. It should be pointed out that if a different method of measuring "liminal values" were used, the above figures might be changed somewhat, but would be expected to hold similarly comparative values.

The above calculations may be reversed, affording a means of calculating and predicting the amount of sulfate ion necessary to precipitate a given iron sol:

$$[SO_4^{--}] = \sqrt[3]{\frac{(k)^P}{\left(\frac{Fe}{P}\right)^2}}$$

where k is about 10^{-1}, P is the purity, and (Fe) the total iron.

The evidence presented above is strictly in accordance with the chemical hydrolytic definition of iron hydrosols, based upon the law of mass action. The theory of preferential ionic adsorption seems unnecessary to explain iron sol behavior, and if there is such a phenomenon as preferential ionic adsorption in these systems, the effects of such adsorption seem to be governed by the law of mass action, as applied to the solution link part of the micelle.

EXPERIMENTAL

In accordance with the hypothesis presented above, the following generalities should be considered:

(1) The purity of a sol, at incipient precipitation, of the chloride type, should increase with dilution.

(2) At incipient precipitation, sols of the weak acid type should have constant purities, independent of dilution.

(3) For two sols of the weak acid type, the difference in their respective purities at incipient precipitation should depend upon the relative values of the dissociation constants of the acids formed; therefore their purities should be nearly equal.

(4) From the liminal value–ion product constant relation, it is evident, if the ideas presented above are correct, that peptization should occur even if sulfate be present, and the greater the concentration of sulfate, the smaller the final obtainable purity, provided the chloride (or other anion) remain constant.

For the purpose of testing these ideas, the peptization experiments shown in table 6 were started.

The ferric hydroxide used in the series given in table 6 was prepared by slow precipitation from the chloride with ammonium hydroxide and then washing daily by decantation with large volumes of water (about 25 liters) for six weeks, until samples of the wash water gave no test whatsoever with equal volumes of 0.1 *N* silver nitrate solution on six successive days. The acids used were the purest obtainable from the Eastman Kodak Co., and were standardized against known sodium hydroxide solution. In all cases there was excess of ferric hydroxide. After standing nine months these solutions were analyzed, after being centrifuged for 60 minutes at about 1000 r.p.m. The iron and organic anions were determined as in the preliminary part described above, the chloride in a similar manner, and the sulfate as the barium salt. The results are given in tables 7 and 8.

In table 8 are shown the results obtained with the same three weak acids but with ferric hydroxide that had been washed only a few times, and so still contained occluded chloride. Anion calculated from normality of acid and final volume.

The results of this last experiment indicated that Mabee's value of 20

(as against the low purity shown in table 7) might be due to the presence of chloride in his sols. Fortunately, there was available in the laboratory some of the iron acetate he used, as well as one of his sols. Both revealed the presence of chloride upon addition of silver nitrate, after heating with nitric acid.

TABLE 6

Peptization experiments

SOL NO.	$Fe(OH)_3$ SUSPENSION	ACID	ACID	ACID	WATER	$M/2$ SODIUM SULFATE
	cc		*N*	*cc.*	*cc.*	*cc.*
1	40	Acetic	0 0853	200	10	
2	40	Acetic	0 0853	150	60	
3	40	Acetic	0 0853	100	110	
4	40	Butyric	0.0871	200	10	
5	40	Butyric	0 0871	150	60	
7	40	Propionic	0 0884	200	10	
8	40	Propionic	0 0884	150	60	
9	40	Propionic	0.0884	100	110	
11	100	Hydrochloric	0 50	15	135	
12	100	Hydrochloric	0.50	25	125	
13	40	Propionic	0.0884	200	0	
15	40	Propionic	0.0884	200	0	
16	40	Butyric	0.0871	200	0	
17	40	Butyric	0.0871	200	0	
18	40	Butyric	0.0871	200	0	
19	40	Acetic	0 0853	200	0	
21	40	Acetic	0 0853	200	0	
22	20	Propionic	0 0884	200	0	
23	20	Propionic	0 0884	200	0	
24	20	Butyric	0 0871	200	0	
25	20	Butyric	0 0871	200	0	
26	20	Acetic	0 0853	200	0	
27	20	Acetic	0 0853	200	0	
28	100	Hydrochloric	0 520	19 2	280 8	
33	100	Hydrochloric	0 520	11 5	288.5	0
34	100	Hydrochloric	0 520	11.5	287 5	1
35	100	Hydrochloric	0 520	11.5	286 5	2
36	100	Hydrochloric	0 520	11 5	285.5	3
37	100	Hydrochloric	0 520	11 5	283 5	5

An iron propionate solution from iron filings and pure acid, oxidized with hydrogen peroxide and centrifuged, gave a purity of 1.1 upon analysis. Similarly, using acetic acid, a purity of slightly less than 1 was obtained.

It is at once apparent that these results are in accordance with the main points outlined above, and hence help to strengthen the hydrolytic point of view of micelle stability, and the chemical reaction ("solubility product" or ion product) idea of sol precipitation. It also seems quite probable that

TABLE 7

SOL	IRON	ANION	PURITY
	Acetate		
	milliequiv per liter	*milliequiv per liter*	
1	114	68 2	1 7
2	141	51 2	2 8
3	135	34 1	4 0
19	148.5	71.1	2 1
20	123	66 1	1 9
21	127 5	71 1	1 8
26	130 5	71 1	1 8
	Butyrate		
4	57	70	0 8
5	66	52 3	1 7
16	82 5	72 6	1 1
17	88.5	72 6	1 2
18	76.5	72.6	1.1
24	52.5	22 6	2.3
25	45 0	23 6	1.9
	Propionate		
7	147	70 7	2 0
8	138	53.0	2.6
9	153	35 4	4 3
13	147	73.6	2.0
15	158	73 6	2.1
22	100 5	73 6	1 3
23	142 5	73 6	1 9
	Chloride		
11	324	30	10 8
12	338	50	6 8
28	346 5	25	13.9
33	366	12 5	29 3

Chloride and sulfate ion

SOL	IRON	ANION		PURITY (Fe) (Cl)
		Chloride	Sulfate	
	milliequiv per liter	*milliequiv. per liter*	*milliequiv per liter*	
33	366.0	12.5	0	29.3
34	339	12.5	1.3	27.1
35	336	12 5	2.5	26 9
36	126	12.5	3.8	10 8
37	(no apparent peptization—clear solution)			10.8

Mabee really studied a mixture of ferric oxychloride sol and ferric acetate sol, and thus found properties intermediate between the two. The differences between two sols of the weak acid type apparently are too small to be significant in view of the fact that this type of sol in general appears to peptize such extremely small amounts of $Fe(OH)_3$.

TABLE 8

SOL	IRON	ANION	PURITY
	milliequiv per liter	*milliequiv. per liter*	
Chloride	241	17	14.2*
Acetate	195	21.7	9.0
Propionate	186	22.1	8.4
Butyrate	180	21.8	8.2

* No Fe_2O_3 residue; all added was peptized.

SUMMARY

1. The purities at incipient precipitation of iron hydrosols are in agreement with the hydrolytic definition of sols.

2. A chemical theory of sol precipitation, based upon the solubility product concept, is supported by the experimental data.

3. Weak acids, such as acetic, propionic, and butyric, bring little more than equivalent amounts of iron into solution, but small amounts of chloride will greatly increase the amount of iron peptized.

4. All the above is in agreement with the chemical-complex theory of hydrosols.

The author wishes to express his appreciation and gratitude to Professors A. W. Thomas and S. J. Kiehl for their friendly criticisms and invaluable suggestions during the development of this subject.

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PHASE CHANGES IN ENZYME SYSTEMS: AZOTASE ACTIVITY IN RELATION TO pH

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The phase rule has seldom been employed in interpreting enzyme behavior. It represents, nevertheless, a relatively simple method of analysis that is often highly determinate. It makes possible distinction between change in number or kind of phase and mere change in phase composition.

This paper will present a phase rule analysis of the abrupt activity–pH function of the nitrogen-fixing enzyme system azotase.[1] General applications to enzyme chemistry and kinetics, whether homogeneous (23, 27, 38) or heterogeneous (2, 7, 12, 13, 15, 16, 17, 18, 25, 34, 35, 37), will be indicated. Azotase will represent a fundamental type case.

PHASE RULE ANALYSIS OF USUAL ENZYME ACTIVITY–pH FUNCTION

The influence of pH on enzyme reactions has been variously explained on some one of the bases that either the enzyme or the substrate is a weak acid or base and that activity is correlated with the concentration of undissociated molecules or positive or negative dissociated molecules, as the case may be (1, 11, 22, 26). The experimental activity–pH curves are

[1] *Azotobacter* possesses a highly specific enzyme system, azotase, capable of catalyzing the fixation of nitrogen gas at ordinary temperatures and pressures Its properties are constant and characteristic, and have been described in detail elsewhere (6). In brief, no activity occurs below a critical concentration of hydroxyl ion of $10^{-8.03}$ M (pH 5.97). Ca or Sr and Mo or V are required for its operation, being replaceable by no other elements. The Michaelis dissociation constant, Km_{N_2}, or nitrogen pressure at half-maximum velocity, is 0.215 atmosphere. Km_{N_2} and the pH limit at 5.97 ± 0.02 are not affected by any known factor, including concentration of calcium or strontium. Specific inhibition by hydrogen ion and oxalate is reversible and non-competitive. Finally, unpublished data indicate that the O/R potential (as imposed upon *Azotobacter* cells by various pressures of oxygen gas) must ordinarily be slightly but definitely lower for maximum azotase activity as compared to nitrate reduction, growth, or any other normal activity of *Azotobacter*. Nitrogen gas is ordinarily fixed by *Azotobacter* in intracellular form only, the amount being directly proportional to the amount of growth. The velocity of fixation becomes solely limited by the velocity of growth (generation time for cell division, or increase in cell mass) only when pH, nitrogen pressure, calcium concentration and O/R potential are all adjusted to values specifically optimal for azotase activity.

very similar to dissociation or dissociation–residue curves. Further emphasis is lent by the fact that enzyme systems usually contain protein-like components, and activity–pH curves likewise resemble the continuous pH functions of the physical properties of aqueous amino acids, polypeptides or proteins, viz., solubility, viscosity, swelling, osmotic pressure, surface tension, alcohol number.

The phases, or physically homogeneous regions, involved in enzyme activity are characterized at equilibrium by variability in chemical composition and constancy in number, without regard to quantity or form. The essential element in the concept of phase is characterization of the properties of each phase by a definite number of degrees of freedom, or parameters (14, 19, 20). At constant temperature and pressure the equilibrium concentrations and ratios of the individual components, dissociated and undissociated, of any one phase, alter continuously over the entire pH range. The number of components and phases remains constant. The simplest type of base–acid equilibrium, occurring in dilute aqueous solution within a single phase at constant temperature and pressure, and first order with respect to all individual components, may be represented, in nomenclature resembling that of Brönsted and Guggenheim (4), by the equation

$$B \rightleftharpoons A + OH^- \tag{1}$$

where B and A are conjugate weak base and acid, differing in charge algebraically by one.

Equation 1 defines a two-component, one-phase system that is trivariant, since by the phase rule $F = C - P + 2 = 2 - 1 + 2 = 3$ degrees of freedom. The mass law dissociation constant contains all individual components:

$$K_B = (A)(OH^-)/(B) \tag{2}$$

Curve I, figure 1, and curve I, figure 2, illustrate graphically the very common function represented by equation 1. Percentage dissociation is plotted against pH and (OH^-) respectively, and a value of (OH^-) existing when the ratio (A)/(B) is unity is arbitrarily chosen as $10^{-7.94}$ M. This value represents attainment of 50 per cent maximum activity in the azotase function. Curves II, III, and IV, figure 1, and curves II, III, and IV, figure 2, present the functions obtained when hydroxyl ion is involved in equation 1 to some number (equation 2, some power) moderately but not greatly different from one, viz., 1/2, 2, and 4. Plots against (OH^-) as well as pH are given because although the latter are more common they are somewhat arbitrary and, in connection with equation 1, less direct (36).

As approximations to these theoretical functions, curves V and VI, figures 1 and 2, show typical, reversible, enzyme activity–pH functions, viz.,

respiration and growth of *Azotobacter* (6), plotted upon a basis of percentage of maximum activity. The differences are of a secondary nature. (OH^-) appears to be involved to a power not far from unity, indicating a relatively simple system. Clark (9) cites numerous references to similar biological pH-functions, enzymic and otherwise. These usual functions have been described as a basis for comparison with the azotase function.

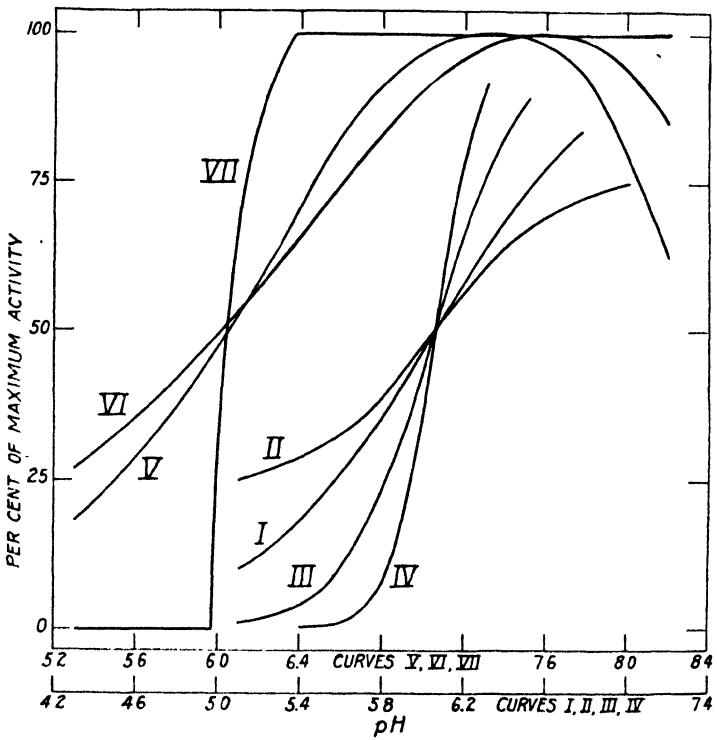

FIG. 1. COMPARISON OF VARIOUS ACTIVITY-pH FUNCTIONS

Curves I, II, III, IV, theoretical curves based on equations 1 and 2, with $K_B = 10^{-7.94}$ and 1/2, 1, 2, and 4 hydroxyl ions, respectively, involved. Curves V, VI, VII, respiration, growth (in nitrate) and nitrogen fixation (by azotase) in *Azotobacter vinelandii*, from data of Burk, Lineweaver, and Horner (reference 6, figure 4).

THE AZOTASE ACTIVITY–pH FUNCTION

The unique activity–pH curve of azotase is reproduced in curve VII, figure 1 (cf. also curve VII, figure 2). The velocity constant of nitrogen fixation is plotted upon the basis of percentage of maximum activity. The distinctive characteristics of the curve upon which the phase rule analysis will be based are as follows.

(1). It approaches a critical threshold pH limit at zero activity in a

manner concave downward, substantially perpendicular. The usual curves, plotted against pH as shown in figure 1, are S-shaped or double S-shaped (bell-shaped), and approach the pH axis asymptotically (concave upward). No finite critical pH is involved, except in certain types of minima to be discussed later. In the plot against (OH^-) the curves intersect the (OH^-) axis at the origin.

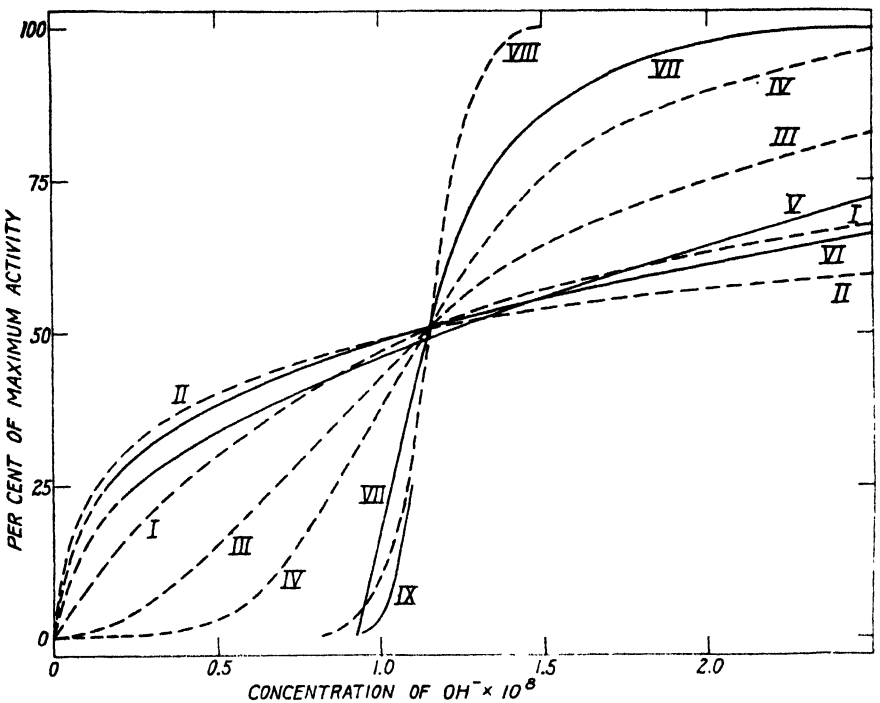

FIG. 2. COMPARISON OF VARIOUS ACTIVITY-(OH^-) FUNCTIONS

Curves I, II, III, IV, VIII, IX, theoretical curves based on equations 1 and 2, with $K_B = 10^{-7.94}$ and 1/2, 1, 2, 4, 16 and 24 hydroxyl ions, respectively, involved. Curves V, VI, VII, respiration, growth (in nitrate) and nitrogen fixation (by azotase) in *Azotobacter*, from data of Burk, Lineweaver, and Horner (reference 6, figure 4).

(2). The azotase function is reversible over an indefinitely extended period of time; this is true even considerably below the pH of zero activity, down to pH 5.0. *A true thermodynamic equilibrium is therefore involved,* approachable from either side of pH 5.97. The usual functions generally show irreversible inactivation in a few minutes or hours at a pH where activity is still 20 per cent of maximum (curve III, figure 3).

(3). The pH limit is a characteristic constant, and has not been observed so far to be changeable beyond ±0.05 pH unit at most, if at all. Usual

functions may often be greatly shifted along the pH axis by various factors. An excellent example is the shifting of the oxygen–hemocyanin dissociation constant one and one-half pH units by 0.5 *M* sodium chloride (figure 3, curves I, IA), or similarly that of oxygen–hemoglobin by various salts

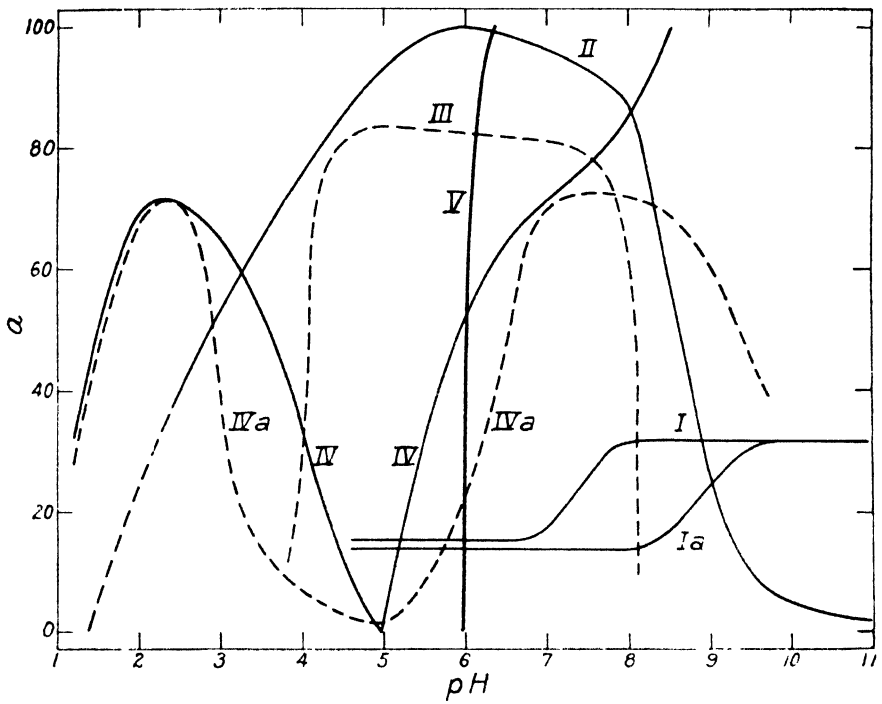

FIG. 3. COMPARISON OF SPECIAL pH FUNCTIONS OBTAINED BY VARIOUS INVESTIGATORS

Curves I and Ia, oxygen affinity constant of hemocyanin of *Busycon canaliculatum*, in presence and absence of 0.5 *M* sodium chloride, respectively, from data of Redfield and Ingalls (reference 31, figures 3 and 4; $a = p_{50} \times 7.5$ mm. mercury). Curve II, relative rate of respiration of *Sarcina lutea*, from data of Rubenstein (reference 32, figure 6). Curve III, sedimentation velocity of hemocyanin of *Helix pomata*, from data of Svedberg and Heyroth (reference 33, figure 5; a = sedimentation velocity $\times 8.22 \times 10^{12}$ cm. per second. Curves IV and IVa, relative concentration of ionized gelatin salt and relative rate of hydrolysis by pepsin (acid to isoelectric point) or trypsin (alkaline to isoelectric point), respectively, from data of Northrup (reference 26, figures 4 and 5). Curve V, relative activity of azotase, from data of Burk, Lineweaver, and Horner (reference 6, figure 4).

(reference 3, figure 191, p. 621). Daniel (10) changed the isoelectric point of gelatin over one pH unit by varying alcohol concentration up to 60 per cent.

(4). The azotase curve shows tremendous molal buffering capacity over

the pH range involved, 5.97 ± 0.02 and 6.37 ± 0.02 (curve VII, figure 1). A change in activity from 0 to 100 (±2) per cent takes place in 0.4 pH unit. Usual enzyme curves require at least one and generally several pH units for only 95 per cent change.

Many observations exist in the literature to the effect that a certain biological process has a characteristic pH limit. Thus Clark (8) showed that certain strains of *B. coli* invariably stopped growing when a pH limit of 4.8 was attained. In cases of this sort, however, the data rarely indicate the manner of reversible approach to the pH axis, especially when very close. For example, in curve II, figure 3, it is suggested that the dotted portion represents a certain amount of irreversible pH effect and that the reversible curve really becomes asymptotic as in the alkaline region.

PHASE RULE ANALYSIS OF AZOTASE ACTIVITY–pH FUNCTION

So far as the writers are aware there is only one interpretation, based, namely, on the phase rule, which is consistent with all four of the above-cited characteristics of the reversible reaction between hydroxyl ion and the inactive azotase residue:

$$A_{OH^-} \rightleftharpoons A_{H^+} + OH^- \tag{3}$$

where A_{OH^-} and A_{H^+} are the active and inactive forms of the grouping in azotase specifically influenced by pH. The charges on A_{OH^-} and A_{H^+} may be positive, zero, or negative, but differ algebraically by the number of hydroxyl ions involved, presumably one (see later).

Equation 3 and curve VII, figure 1, describe a two-component system which is univariant under ordinary experimental conditions, where temperature, pressure, and total cellular azotase concentration (A_{OH^-} and A_{H^+}) are held constant, and the state of the system is defined by the hydroxyl ion concentration of the external medium, no A_{OH^-} existing below about pH 5.97, no A_{H^+} existing above this value. According to the phase rule the number of phases existing when the system is in equilibrium at pH 5.97 is three, thus: $P = C - F + 2 = 2 - 1 + 2 = 3$. One phase, containing the hydroxyl ion, is aqueous, and the other two, consisting of A_{OH^-} and A_{H^+}, respectively, are therefore non-aqueous, either liquid, solid, or surface phases. It is assumed for the present that curve VII, figure 1, is strictly perpendicular and that the two non-aqueous phases are therefore pure components or compounds of fixed composition. The possibility that A_{OH^-} varies somewhat in composition between pH 5.97 and 6.37 will be considered shortly.

Since in heterogeneous equilibrium the absolute mass or quantity of one phase does not influence the composition of another phase, (A_{OH^-}) and (A_{H^+}) do not appear in the mass law dissociation constant:

$$K = (OH^-) = 10^{-8.03} \tag{4}$$

In view of the equilibrium $(H^+)(OH^-)/(H_2O)$ in the aqueous phase, equations 3 and 4 might be written, so far as available experiments decide,

$$A_{H^+}(\text{non-aq}) \rightleftharpoons A_{OH^-}(\text{non-aq}) + H^+(\text{aq}) \tag{3'}$$

$$K' = (H^+) = 10^{-5.97} \tag{4'}$$

This ambiguity occurs commonly in base–acid equilibria and must be resolved by independent evidence (reference 9, 2nd ed., 1925, pp. 29, 306), e.g., migration experiments. Alteration of K in equation 4 (or K' in 4′) to an extent minute or otherwise, although unobserved so far, is theoretically possible under the phase rule, as a function of temperature, total pressure, or the chemical composition of A_{OH^-}.

Comparable equilibria

The heterogeneous equilibrium of equations 3 and 4 is comparable to well-known univariant gas–solid equilibria involving salt hydration. Thus, with, e.g., anhydrous copper sulfate and water vapor, no hydrate is formed at constant and ordinary temperatures until a certain critical water vapor pressure is reached, about 4.5 mm. This is the dissociation pressure of the monohydrate, at which point the anhydrous salt is all converted into the new compound, the monohydrate, before further rise in the equilibrium vapor pressure may occur, two solid phases (three altogether) existing during the meantime.[2] The equations representing these phenomena of critical phase change, corresponding to equations 3 and 4, are:

$$CuSO_4 \cdot H_2O(s) \rightleftharpoons CuSO_4(s) + H_2O(g) \tag{5}$$

$$K_{diss} = (H_2O) = 4.5 \text{ mm. at } 50°C. \tag{6}$$

Here $F = C - P + 2 = 2 - 3 + 2 = 1$. In the system solid mono- and di-calcium phosphates in aqueous equilibrium at constant temperature and pressure at a given pH, the slightest change of pH in either direction results in the complete conversion of one solid to the other. This system is perhaps more analogous to the azotase system than salt hydration in view of the nature of the independent variable (pH) and the known rôle of calcium

[2] In Bayliss' phase rule analysis of the system hemoglobin–oxyhemoglobin–oxygen (reference 3, p. 617, last paragraph) three phases and two components were assigned in the equation $F = C - P + 2 = 2 - 3 + 2 = 1$, and it appeared therefore that the system was formally comparable to the univariant system $CaCO_3$ (s)–CaO(s) –CO_2(g) (or, similarly, the case of salt hydration illustrated). This was taken to be anomalous inasmuch as bivariance was observed experimentally. However, from the nature of the dissociation curves (reference 3, pp. 620, 621) oxygen combines with hemoglobin at *all* pressures and hence hemoglobin and oxyhemoglobin occur in one and the same composition-varying phase, so that $F = 2 - 2 + 2 = 2$. This leaves no basis for the alternatives of either the existence of three components, or non-applicability of the phase rule to microheterogeneous systems.

in fixation. Amylase activity apparently involves an essential organic calcium component also (24).

The pH *region 5.97 to 6.37*

The azotase function appears to require some 0.4 pH unit to change reversibly from 0 to 100 per cent activity. Slight non-homogeneity of phase may be involved; it is well-known that even under equilibrium conditions the vapor pressure of liquids depends slightly upon the size of the droplets; the solubility of solids upon the size of the particles; the melting point without decomposition may vary a perceptible fraction of a degree; surfaces may depart somewhat from complete homogeneity, varying perhaps in curvature; and secondary factors ordinarily neglected may affect certain phase rule applications. Mathematically considered, the magnitude of the region of phase change depends upon the phase spaces involved, in the sense employed in statistical mechanics. Zero velocity at pH 5.97 represents in any case complete conversion of A_{OH^-} to A_{H^+}, and the attainment of maximum velocity above pH 6.37 complete conversion of A_{H^+} to A_{OH^-}, within experimental error.

It is scarcely possible that

$$A_{H^+}(\text{non-aq}) + OH^- \rightleftharpoons A'_{OH^-}(\text{non-aq}); \text{ phase change, pH } 5.97 \quad (7)$$

and

$$A'_{OH^-}(\text{non-aq}) + n_{OH^-} \rightleftharpoons A_{OH}\ (\text{non-aq}); \text{ non-aqueous solution, pH } 5.97 \text{ to } 6.37 \quad (8)$$

where A_{H^+} is converted at pH 5.97 into a new but inactive non-aqueous phase, A'_{OH^-}, which becomes active upon further combination with, or solution of, aqueous OH^- ions over the region to pH 6.37, when all A'_{OH^-} is converted into completely active A_{OH^-}. It is evident, comparing the upper portions of curve VII, figure 2, and curves IV or VIII, that the value of n in equation 7 must be much larger than in the usual enzyme dissociation, and, moreover, for the portion below 50 per cent activity that curve VII does not represent merely dissociation with some large power of n. If one plots the logarithm of the ratio of the concentrations of undissociated and dissociated molecules of an electrolyte against pH a line is obtained whose slope represents n, the number of hydroxyl ions involved in the dissociation. Such a plot of the azotase function does not yield a uniformly straight line but one which varies continuously, indicating that n varies. Between 6.3 and 6.15 n appears to possess a fairly constant value of about 6, but at pH 6.0, where activity is only about 25 per cent of maximum, it becomes 12, at 5.98, 31, and at 5.97 substantially infinite.

PHASE CHANGE ALTERNATIVES

A curve at relatively low activities, lying between curves VIII and IX, figure 2 (n = 16 and 24, respectively), would cross curve VII within experi-

mental error of measurement of zero activity (about 1 per cent of maximum, where $A_{H^+}/A_{OH^-} = 100$). The azotase pH *limit* 5.97 might thus be explained homogeneously,

$$A_{OH^-} \rightleftharpoons A_{H^+} + 20\,OH^- \tag{9}$$

$$K'' = (OH^-)^{20}(A_{H^+})/(A_{OH^-}) \tag{10}$$

except for there being no chemical precedent for a molecule with some twenty (basic) groups titratable at the same pH. (The problems of limit (equation 9) and transition range (equation 7), each involving large values of n, are to be clearly distinguished.)

Similarly, A_{OH^-} and A_{H^+} might differ greatly in molecular weight.

$$A_{OH^-} \rightleftharpoons 20A_{H^+} + nOH^- \tag{11}$$

$$K''' = (OH^-)^n(A_{H^+})^{20}/(A_{OH^-}) \tag{12}$$

Most properties of a molecule must be considered quantitatively as properties of the whole molecule and not as the sum of the properties of the various composing groups or atoms. It is thus conceivable that the molecule within the azotase system specifically affected by OH^- is active only when possessed of a minimum molecular weight. Here again, however, numerous groups all dissociating reversibly at approximately pH 6.0 would have to be involved, for which there is no chemical precedent. Svedberg and Heyroth (33) showed that the sedimentation velocity of hemocyanin from *Helix pomatia* decreases about tenfold between pH 4.8 and 3.8 (curve III, figure 3) and is accompanied by a roughly parallel decrease in molecular weight. Actually, however, the curve is reversible only in the earliest stages at the higher pH values; several hours exposure at 3.4 results in 25 to 75 per cent permanent change.

Certain properties of ampholytes, electric charge and cataphoretic or membrane potential, approach abrupt minima substantially linearly as a function of pH, as illustrated in curve IV, figure 3, for gelatin. In the case of hemoglobin the electric charge involved decreases reversibly to zero between pH 8.4 and the isoelectric point 6.8, where it presumably changes abruptly to positive (26). Compared to curve VII, figure 1, however, such curves extend over a much greater pH range and do not appear capable of offering an alternative explanation for the assigned phase change in azotase, although they may represent accompanying phenomena. Moreover, the corresponding enzyme activity curves, e.g. curve IVa, figure 3, approach their minima concaved upward in the normal continuous manner.

DISCUSSION

The phase rule involves great generality and formality in one sense, but also high specificity, as a means of classifying a great variety of type reac-

tions, homogeneous or heterogeneous. It makes possible distinction between change in number or kind of phase and mere change in phase composition. The use of phase rule analysis will quite possibly be imperative[3] in certain cases of enzyme reaction velocity or enzyme stability where inhibitors, accelerators, carriers, and substrates sometimes appear to act only above certain critical limiting concentrations. Thus Quastel and Whetham (29) find for certain dehydrogenases the equation $v = k \log (S/C)$ where the velocity $v = 0$ when substrate concentration S = critical concentration C; by phase rule analysis there would appear to be a bivariant two-component, two-phase system, with an inactive non-aqueous phase invariant in composition occurring below the critical concentration and an active substrate–solution phase above it (cf. equations 7, 8).

In the case of nitrogen fixation, quite possibly the very nature of the reaction involved accounts for the phase change requirement. The dissociation energy of the nitrogen molecule is some $8\frac{1}{2}$ volts or more (200,000 calories). This is enormously greater than the heats of activation of most enzymic reactions, which are rarely more than 10,000 to 20,000 calories. Generally considered, heterogeneous catalysis is much more effective than homogeneous catalysis in causing unusually unreactive molecules to react. Cannan (7) has reviewed the evidence for the view that the catalytic action of enzymes is restricted to certain surface areas. Quastel's (28, 30) modified electric field theory of dehydrogenase activity and enzyme specificity provides for surface differentiation into specific areas or regions of unequal activity. Langmuir (19) has recently developed a detailed extension of the phase rule to include surfaces of the most varied types, active and inactive, in which a surface may consist of several phases, differing in structure or composition, but not size or shape. The phases may thus be submicroscopic, as well as microscopic or macroscopic as in ordinary phase rule applications. This point is important in view of the fact that the *Azotobacter* cell is only about 2000 A.U. in diameter and the

[3] However, McBain (21), in common with Loeb, Sörensen, Perrin, Pauli, and Smoluchowski, holds that by phase rule a solution of reversible colloid, no matter how complicated, may be considered to behave toward external equilibria as a single phase. Buchner (5) concludes that while a colloidal solution may be regarded as either a one- or two- (or more) phase system, microheterogeneous systems in general seldom involve the formation of new phases and hence that the concept of phase will rarely be useful in connection therewith. He reviews various opinions on the nature of the concept phase and, while agreeing that heterogeneity may be considered relative and not absolute (depending upon the smallness of particles and roughness of observation), inclines to the single phase view. On the other hand, the three-phase system azotase indicated in this paper throws new light on the problem, and strengthens the view that enzyme systems may consist of more than one phase, and that for some enzymes equation 1 might represent a two-component, two-phase, bivariant system rather than a two-component, one-phase, trivariant system.

enzyme systems within it of course very much smaller. It is not necessary, in fact, that the A_{OH^-} and A_{H^+} phases consist of more than some several hundred molecules, enough to sustain the statistically based, thermodynamic equilibrium observed experimentally.

SUMMARY

1. Azotase (nitrogen-fixing) activity in *Azotobacter* varies with pH abruptly. A characteristic zero limit at 5.97 is approached *reversibly* and perpendicularly. Phase rule analysis implicates a two-component heterogeneous system with three phases in equilibrium at the critical pH: aqueous, active non-aqueous, and inactive non-aqueous. The active (basic) component exists above the critical pH, the inactive (acidic) one below. Slight phase non-homogeneity may occur between pH 5.97 and 6.37. Interpretations of the abrupt pH function, alternative to phase change, such as normal acid–base dissociation, large molecular weight change, multiple basicity, and minimal charge or potential difference have been discarded as inconsistent with one or more characteristics of the reaction.

2. Phase rule applications to microheterogeneous systems, surfaces, and problems of general enzyme reaction velocity and stability have been briefly indicated.

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EFFECTS OF ALPHA PARTICLES ON AQUEOUS SOLUTIONS[1]

I. The Decomposition of Water

II. The Oxidation of Ferrous Sulfate

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There is much evidence to show that the primary action in gases due to alpha radiation is ionization. Since it is found true in gases at high pressures, it might therefore be expected to be true in many liquids. Water was the first liquid investigated; however, the idea of ionization was not present in the earliest work. In 1907, Cameron and Ramsay (1) studied for the first time the decomposition of water by radon. There soon followed a series (2, 8, 19) of investigations out of which evolved some experiments which practically ended further study of this particular reaction. The experiments were performed by Duane and Scheuer (3) in the laboratory of Madame Curie. They found that 2.9 cc. of gas are formed per curie hour when carefully prepared distilled water is irradiated with alpha rays. Water molecules were decomposed with a yield of nearly one molecule per ion pair. The gas formed, however, was not an electrolytic mixture of hydrogen and oxygen, but always contained an excess of hydrogen. They concluded that hydrogen peroxide was formed by the secondary action of nascent oxygen on water. Kernbaum (8) had observed the same phenomena in an earlier experiment. He measured the amount of hydrogen peroxide in the irradiated water and found a sufficient quantity to account for the excess hydrogen.

In 1911, Lind (10) reported some results on the irradiation of liquid hydrogen bromide and solutions of potassium iodide. Recently Lind and Ogg (16) have cited some further results on the decomposition of liquid and gaseous hydrogen bromide. Liquid hydrogen bromide was decomposed with a yield of 2.6 molecules per ion pair, which is remarkably close to the yield of 2.8 for gaseous hydrogen bromide.

The author wishes to report here some further observations on the decomposition of water and some new studies on the oxidation of aqueous solu-

[1] From a thesis submitted by Carl E. Nurnberger to the Faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

tions of ferrous sulfate. In particular, it is desirable to follow the reactions by measuring quantitatively the gas produced and the substances changed, and to express them in terms of the ionization produced by alpha particles emitted from the radioactive gas, radon.

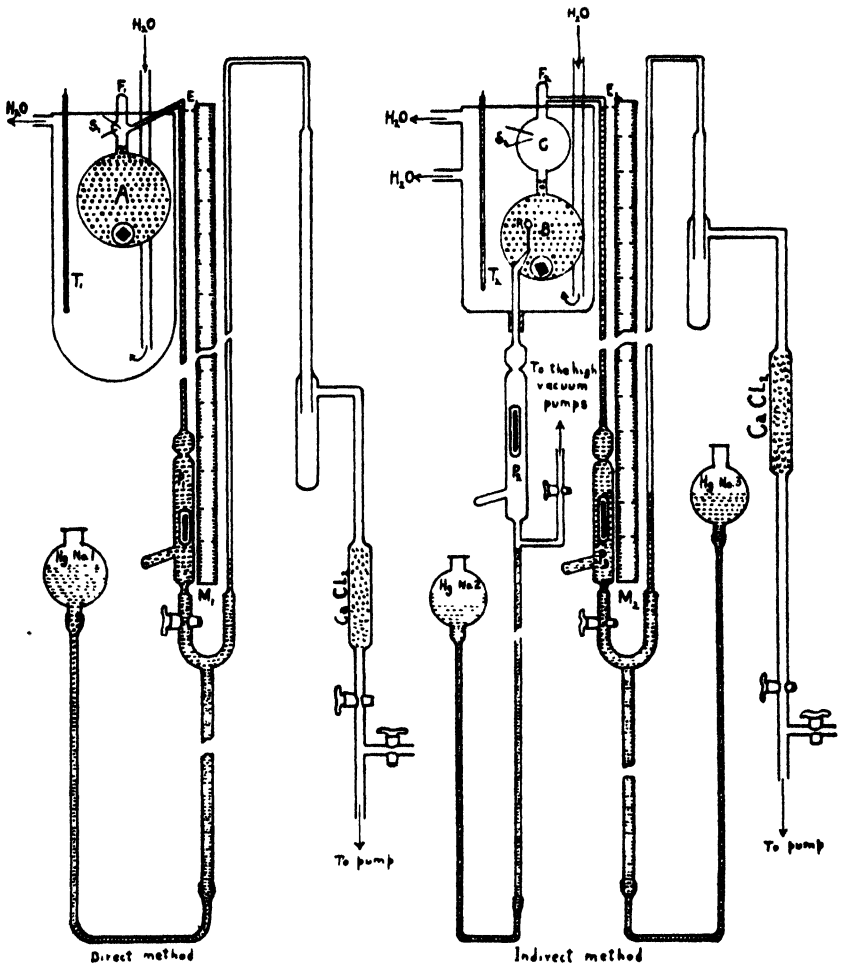

FIG. 1. APPARATUS FOR THE STUDY OF THE EFFECTS OF ALPHA RAYS ON SOLUTIONS

EXPERIMENTAL

Two different experimental methods have been used and the apparatus for both is shown in figure 1. The methods are designated the direct and the indirect method. In the former, radon is placed in direct contact with the liquid, where a part of it is dissolved and the rest remains in the gas volume above the liquid surface. In the latter method, radon is confined

to an alpha-ray bulb (11) immersed in the liquid. Radon in the direct method distributes itself between the liquid and the gas volumes, and the effective amounts in each will depend upon their relative volumes and the area of the liquid surface. The first factor determines the quantity of radon dissolved in the liquid where complete absorption of alpha particles occurs; the second factor determines that portion of the alpha particles which have their source in the gas volume, but which strike the liquid surface. The latter may be partially eliminated by the use of irradiation chambers wherein the liquid surface is small. The dotted portion of chamber A (figure 1, direct method) indicates the liquid volume. The liquid surface rests in the tube F, whose cross-sectional area is about 0.1 sq. cm. The liquid volumes for both methods (A and B) were varied from 15 cc. to 60 cc. for different experiments. The gas volumes (F, direct method, and F_2 plus g, indirect method) were varied from 1 to 5 cc. and from 5 to 10 cc. for the direct and indirect methods, respectively.

Radon, which had previously been collected, purified,[2] and stored in small glass bulbs of about 4-mm. diameter, was brought into the apparatus through a side tube of the traps P_1, P_2, and P_3. The side tube is then sealed and the entire system is evacuated, after which mercury is brought into the manometer (M_1 and M_2, figure 1) to a point above the stopcocks. The radon gas is released directly into the reaction chamber (A and F_1, direct method; B, C, and F_2, indirect method), when the storage bulb is broken. The storage bulb is broken when struck by an iron-glass capsule which had been raised a few centimeters above the bulb by an electromagnet and then allowed to fall. Mercury is then raised to a fixed point near the top of the left-hand side of the manometer. All of the radon is thus confined to the reaction chamber. In the other side of the manometer, which is open to the atmosphere, the mercury surface rests near the bottom at the beginning of the experiments. The gas volume is kept constant by having the stopcocks immediately below the traps closed except when pressure observations are taken. The strengths of the radon storage bulbs were determined beforehand by a careful determination of their gamma-ray activity as compared to the activity of two standard radium preparations.

The alpha-ray bulbs (R, figure 1) were located to one side of the chamber B so that they were protected against breakage when samples of the irradiation liquids were removed. Radon was confined to the alpha-ray bulbs when the gas had been released in the trap P_2, as described previously, and mercury had been raised to the topmost point of the capillary tube sealed to the bulb. The mercury surface maintained this position without fluctuating much in either direction.

[2] The radon gas was obtained from the Radium Emanation Plant in the Cancer Institute of the University Hospital, Minneapolis.

Clean apparatus, particularly the reaction chamber, is absolutely necessary to obtain consistent results. All substances are probably attacked in one way or another by the rays from radioactive elements. Usually gases are evolved and various forms of impurities are left in the system. In particular, stopcock grease gives off organic gases and, in order to eliminate them, all stopcocks were situated so as not to come in direct contact with radon. Impurities in the liquid chamber may inhibit or accelerate the action of alpha rays and therefore should be eliminated. The entire glass system was thoroughly cleaned and dried preceding each experiment.

The reaction chambers were immersed in a constant temperature water bath. The temperature of the bath was set a few degrees below room temperature in order to eliminate partially condensation of the liquid vapor in the manometer. The liquids were stirred constantly during each experiment by the motion of a round glass bead. The soft iron core of the bead was alternately attracted and released by an electromagnet about twenty times per minute. This arrangement for stirring the liquids proved to be of much help to keep the liquid and gas volumes constant during the evacuation of the system. Without the stirrer large bubbles of gas formed in the liquid. When they were released, drops of liquid were carried with them into the manometer. However, when the stirrer was operating, the gas bubbles were released when small and practically none of the liquid was taken from the reaction chamber.

The gaseous mixture evolved by the rays was exploded by producing a spark between the electrodes S_1 and S_2 (figure 1). In the first experiments platinum wires were used for the electrodes. Irregularity in the pressure during sparking was observed. The gas remaining after several explosions, presumably hydrogen, would on further sparking disappear almost entirely, only to reappear at the next explosion. This troublesome feature was partially eliminated by saturating the system with hydrogen before the experiment began; however some irregularities still remained. They were finally eliminated by using tungsten instead of platinum electrodes.

The irradiated water was collected from a laboratory still and was further purified by repeated distillations in an all-Pyrex glass still. The water was placed immediately in the irradiation chamber and subjected to a partial vacuum for at least two hours before the experiment began. The initial gas pressure was in most experiments not more than 30 mm. of mercury. Even though the surface area of the water was small, about 0.1 sq. cm., most of the absorbed gases were removed, owing to the continuous stirring. After this preparation the water was ready for irradiation and no gases other than those evolved by the rays came in contact with it. Some preliminary measurements on the conductivity of the water gave 3×10^{-6} mhos.

Aqueous solutions of ferrous sulfate, when irradiated with x-rays, were

first studied by Fricke and Morse (4). The results of their experiments suggested the possibilities of a similar study using alpha radiation instead of x-rays. Solutions for irradiation with alpha rays were made from a stock solution of 0.5 molar ferrous sulfate in 0.8 normal sulfuric acid, and were standardized by titrating with a standard solution of potassium dichromate. Chemically pure potassium dichromate was recrystallized three times and dried two days at a temperature of 110°C. The titration measurements were made according to the method of Kolthoff and Furman (9). To 5 cc. of the solution was added 50 cc. of 0.8 N sulfuric acid. The mixture was stirred and titrated with potassium dichromate from a burette calibrated to read 0.05 cc. accurately and which could be estimated to 0.02 cc. The concentration of each solution was tested immediately before and after each experiment to avoid errors due to spontaneous changes which might occur. At least two independent titrations were made on each sample, and their average value was used to calculate the per cent of ferrous sulfate changed.

RESULTS

I. The decomposition of water

The decomposition of water by alpha rays was studied primarily because it offered a means of standardizing the apparatus by a comparison of the results obtained with it and the results of earlier work, and because it might be used as a method of measuring the transmission of alpha-ray bulbs. This method, to the author's knowledge, has not been used before, and therefore it will be described in detail later in the paper.

The results of one experiment, selected from a large group on the irradiation of water by radon dissolved in the water, are recorded in the top of table 1. The gas volume was kept constant and the gas pressure was observed at regular intervals immediately before and after the explosion of the gaseous mixture. The temperature of the reaction vessel remained constant. All gas pressures and volumes recorded in table 1, and in all tables which follow, are expressed in millimeters of mercury and cubic centimeters at 0°C. and 760 mm. pressure, respectively. The initial quantity of gas in the reaction chamber has been subtracted from all later volumes. The last value of V is, except for certain corrections which shall be discussed later, the total quantity of gas produced by the rays. V_H is practically all hydrogen and represents an excess over the amount which results from the reaction, $2H_2O = 2H_2 + O_2$. V' is equal to V plus an amount of oxygen equivalent to the excess hydrogen.

The course of the reaction is demonstrated in figure 2. The per cent of radon decayed was calculated from the Kolowrat tables. The per cent of completed reaction is equal to $V'/V_\infty \times 100$, where V' is defined in the

TABLE 1

Gas yield in the decomposition of water by radon

DAYS	T_W	p_1	p_2	v_1	v_2	V	V_H	V'	PER CENT V_H	PER CENT RADON USED	$\frac{V'}{V_\infty} \times 100$
Direct method											
Water volume = 19.0 cc.; gas volume = 4.33 cc.; initial quantity of radon = 83.0 mc.											
0.00	20.4	39.1	35.6	0.207	0.188						
0.15	20.6	92.2	44.5	0.487	0.235	0.299	0.047	0.322	15.6	2.6	2 4
0.71	20.7	260.1	54.6	1.376	0.289	1.440	0.101	1.495	6.7	11.9	10.9
0.96	20.3	160.3	41.8	0.848	0.221	1.999	0.033	2.015	1.6	15.8	14 9
1.17	20.7	120.1	42.0	0.635	0.220	2.413	0.034	2.430	1.4	18.9	17 9
1.69	20.5	218.1	41.8	1.154	0 221	3.345	0.033	3.361	0.9	25.9	24 7
2.15	20.2	187.4	40.0	0.991	0 217	4.315	0.029	4.329	0.6	31.8	31.8
2.58	20.2	170.4	39.0	0.899	0 206	4 997	0 018	5.006		37 2	36.8
3.08	20.1	177.0	40.0	0.936	0 217	5.727	0.029	5.741	0.5	42 6	42.2
3.64	20.6	171.0	39.0	0.905	0.206	6.415	0.018	6.415		47.9	47.2
4.14	20.6	151.0	36.0	0.799	0.191	7 008	0 003	7.009		52 4	52.2
4.67	20.8	148.0	33.0	0.783	0.175	7 600		7.600		56 5	55 9
5.67	20.8	210.0	37.0	1 111	0 196	8 536	0 008	8.540	0.1	64 0	62.7
6 77	20.4	192.0	33.0	1 016	0.175	9.356		9.356		70.5	68 8
7.17	20.4	145.0	30.0	0.767	0.159	9.948		9.948		72.5	73 0
8 27	20.4	143.0	33.0	0 756	0.175	10 54		10.54		77.4	77.4
Indirect method											
Water volume = 15.9 cc.; gas volume = 4.33 cc.; initial quantity of radon = 69 1 mc.											
0.00	22.0				0 000						
0.72	22.6	12.6	3.2	0.154	0.039	0.154	0.039	0.173	25.5	11.8	6.8
1.83	22.2	38 4	19.9	0.469	0 243	0.584	0.243	0.705	41.6	28.3	27.7
2.99	21.8	41.3	18.4	0 505	0.225	0.846	0.225	0.958	26.6	41.6	37.5
3.89	22.6	37.1	18.6	0.453	0.227	1.073	0 227	1.186	21.1	50.0	46.5
4.81	21.8	33.4	17.5	0.408	0.214	1 254	0.214	1.361	17.0	57.8	53.4
5.97	22.0	33.2	17.3	0.405	0.211	1.445	0.211	1.550	14.6	65.8	60 6
6.99	21.9	31.1	15.6	0.380	0.190	1 614	0.190	1.709	11.7	71.4	66.9
8.21	22.0	25.5	16.0	0.311	0.195	1.735	0.195	1.832	11.2	77.1	71.8
9.94	21.8	27.4	12.5	0.335	0.153	1.875	0.153	1.951	8.1	83.0	76.5
11.01	21.7	21.4	13.4	0 262	0.164	1.984	0.164	2.066	8.2	86.0	81.0
13.98	22.4	28 1	12.5	0.343	0.152	2 163	0 152	2.239	7.0	91.5	87.8

p_1 = gas pressure before each explosion.
p_2 = gas pressure after each explosion.
v_1 = gas volume before each explosion.
v_2 = gas volume after each explosion.
V = sum of the gases produced in the intervals between explosions.
V_H = gas left in the reaction chamber after each explosion.
$V' = V + \frac{1}{2} V_H$.
$\frac{V'}{V_\infty} \times 100$ = per cent of completed reaction.
T_w = temperature of the water bath.

preceding paragraph, and V_∞ is the total quantity of gas which would have been produced if all of the radon initially dissolved in the water decayed. V_∞ is calculated from the total gas yield per millicurie as observed at the end of the experiment.

The results agree in the main with the observations of earlier work. The per cent of radon decayed and the per cent of completed reaction (figure 2) are in approximate agreement throughout the experiment. This is in accordance with the general law deduced by Cameron and Ramsay (1) that the rate of production of gas is proportional to the quantity of radon dissolved in the water. The per cent of excess hydrogen, which is equal

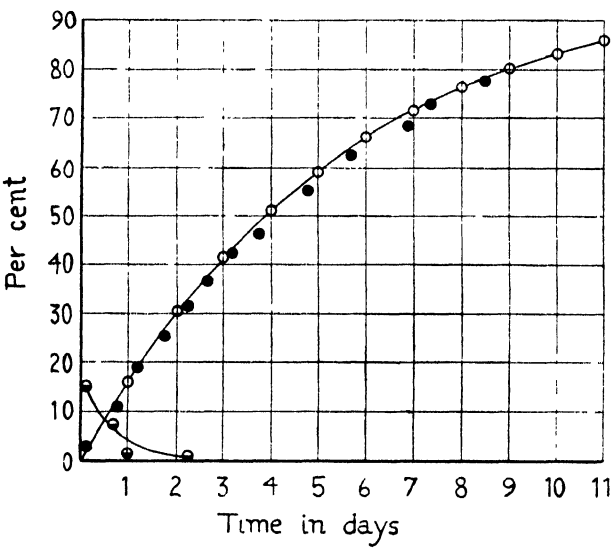

FIG. 2. DECOMPOSITION OF WATER BY RADON (DIRECT METHOD)

○ per cent of radon destroyed; ● per cent of completed reaction; ◒ per cent of excess hydrogen.

to $\frac{V_H}{V} \times 100$ (table 1), decreases as the experiment proceeds, as observed by Duane and Scheuer (3). They explain the decrease as existing when the quantity of hydrogen peroxide formed by the secondary action of nascent oxygen on water reached an amount such that its rate of decomposition, both spontaneous and that caused by the rays, is equal to its rate of formation.

The most marked departure from the results of Duane and Scheuer occurs in the quantity of gas produced per millicurie of radon destroyed as measured experimentally. Their yield is 0.383 cc. per millicurie, while in table 1 the yield is equal to 0.164 cc. per millicurie. The discrepancy was expected, since their value refers to complete absorption of all alpha-rays in

the water, to complete evolution of the hydrogen and oxygen to the gas phase, and without any recombination of the gases. These conditions cannot be had experimentally when the direct method of procedure is used, and therefore, the yield of 0.164 cc. per millicurie is too low.

The distribution coefficient of radon in water at various temperatures (6) has been determined. In particular, at 20.5°C. the coefficient is equal to 0.248. The initial quantity of radon in water and in the gas is given by the formulas,

$$E_0 = E_w + E_g$$

and

$$E_w/E_g = V_w/V_g\ \alpha$$

where E_0 is the total initial amount of radon, E_w is the initial amount dissolved in the water, E_g is the initial amount dissolved in the gas, α is the distribution coefficient, and V_w and V_g are the water and gas volumes, respectively. Application of these formulas to the results recorded in the first part of table 1, gives 43.3 mc. of radon dissolved in the water and 39.7 mc. distributed in the gas. Since 77.4 per cent of the radon was destroyed, 33.5 mc. and 30.7 mc. were destroyed in the water and in the gas, respectively.

The amount of hydrogen and oxygen absorbed by the water is not indicated directly, but can be calculated from the partial pressures of the oxygen in the following manner. When the gaseous mixture is exploded, practically all of the oxygen and an equivalent amount of hydrogen is removed from the water, and hydrogen alone is left in the reaction chamber. This assertion is substantiated by the experimental fact that the gas pressure decreases to a constant value even though the gases were sparked many times thereafter. The amount of oxygen dissolved in the interval between explosions is determined from its average partial pressure in the interval and its solubility in water (0.0286 cc.). There were fifteen explosions in the particular experiment recorded in table 1. A total of 0.464 cc. of oxygen and the equivalent amount, 0.928 cc., of hydrogen, was removed from the water. This oxygen and hydrogen should be added to the total yield, the last value of V', recorded in table 1.

The third correction to be applied to the gas yield results from the recombination of hydrogen and oxygen due to the ionization in the gas by alpha particles and recoil atoms. This particular reaction has been investigated by Scheuer (18), Lind (12), Lind and Bardwell (13), and others. Lind found that for each pair of ions 3.85 molecules of water are formed. Therefore, to determine the quantity of gas used in the formation of water, the intensity of ionization in the gas must be known. The number of ion pairs, which depends upon the average path of the alpha particles, is

difficult to obtain, owing to the irregular shape of the reaction chamber, a major portion of which is cylindrical. Lind and Bardwell (14) have tested a formula for the average path of alpha particles in small spheres and found the average path to be 0.61 r, where r is the radius of the sphere. Lunn extended calculations to geometrical forms other than spheres, and concluded that the formula is applicable to cylinders whose lengths are not greater than their diameters by a factor of 10. These cylinders are treated as spheres of equal volumes. Accordingly, the formula, $\bar{p} = 0.61\ r$, is applicable to the major part of the reaction chamber described in figure 1.

The total number of ion pairs produced in the gas is equal to

$$n \times E_0 (1 - e^{-\lambda t}) \times 2.4 \times 10^4 \times \bar{p} \times i \times \frac{P}{760} \times \frac{\alpha + \alpha}{\alpha}$$

where n is the number of alpha particles emitted when 1.0 mc. of radon in equilibrium is destroyed [5.34×10^{13}, (5)]; $E_0(1 - e^{-\lambda t})$ is the amount of radon destroyed in the gas phase; 2.4×10^4 is the number of ion pairs per alpha particle per centimeter of path in air at 0°C. and 760 mm. pressure; $\bar{p}$ is the average path of the alpha particles; i is the specific molecular ionization of the gaseous mixture and is equal to 0.52 when referred to air as unity; P is the gas pressure; and $\frac{\alpha + a}{\alpha}$ (15) is a factor which includes the effects of recoil atoms. For the particular reaction chamber and experiment described in table 1, $\frac{\alpha + a}{\alpha}$ is equal to approximately 1.9. Evaluation of the expression gives 40.5×10^{17} ion pairs. Since 5.76 molecules of $H_2 + O_2$ are recombined per ion pair, then

$$\frac{40.56 \times 10^{17} \times 5\ 76}{2.705 \times 10^{17}} = 0.5$$

or 0.5 cc. of gas was lost, owing to the ionization produced by alpha particles and recoil atoms.

The total quantity of gas produced takes the value 12.4 cc. (0°C. and 760 mm. pressure) when the gas lost by absorption in the water and recombination in the gas phase is added to the final value of V' in table 1. The new yield per millicurie of radon destroyed in the water is equal to 12 4/33.5, or 0.371 cc. per millicurie.

The gas yield becomes more significant in the theory of ionization and chemical reaction when expressed in terms of molecules reacting per ion pair. It is commonly expressed as M_{H_2O}/N where M_{H_2O} is the number of water molecules decomposed and N is the number of ion pairs produced in the water. M_{H_2O} is equal to $V \cdot 2/3 \cdot 2.705 \times 10^{19}$, where V is cubic centimeters of gas produced per millicurie destroyed, 2.705×10^{19} is Loschmidt's

number, and the factor 2/3 is used since two molecules of H_2O decomposed gives three molecules of $H_2 + O_2$. N is equal to 1.78×10^{13} $(1.67 + 1.83 + 2.37) \times 10^5 \times i$, where 1.78×10^{13} is the number of alpha particles emitted when 1 mc. of radon is destroyed, $(1.67 + 1.83 + 2.37) \times 10^5$ is the number of ion pairs produced by one alpha particle from each of the three sources, radon, radium A, and radium C in air under standard conditions, and i is the total specific ionization of water and is equal to 0.82 when referred to air as unity. Evaluation of M_{H_2O}/N gives 0.78. This is below the range of values, 0.86 to 1.02, of Duane and Scheuer (3). Other experiments in addition to table 1, gave M/N values consistently less than Duane and

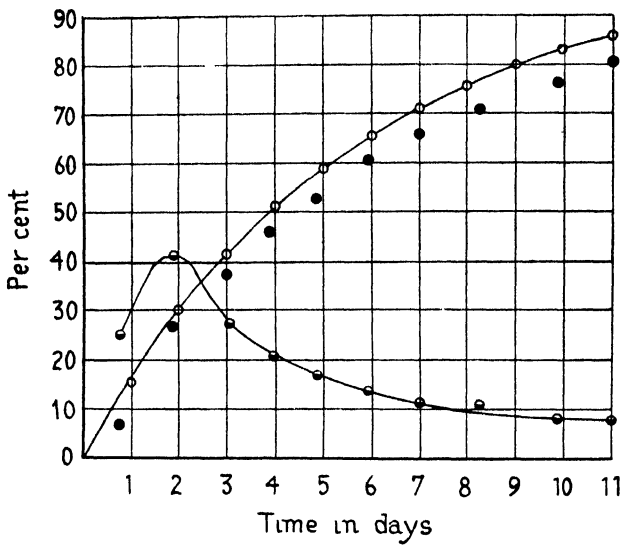

FIG. 3. DECOMPOSITION OF WATER BY RADON (INDIRECT METHOD)

○ per cent of radon destroyed; ● per cent of completed reaction; ◒ per cent of excess hydrogen.

Scheuer's. The discrepancy is probably insignificant, for in systems where large quantities of water are used, the heterogeneous equilibrium of the gases depends upon factors which are difficult to correct.

In the calculation of the gas yield it was assumed that radon is in radioactive equilibrium with its decay products when the experiments began, and furthermore, that radon dissolved quickly in the water. Actually, equilibrium is not reached until about five hours after the experiment begins, so that the alpha particle emission is less for this part of the experiment than it would be if equilibrium really existed. There is, however, no consistent lag in the gas yield during the first few hours, and therefore the errors introduced by the assumptions are negligible.

Quantitative measurements of the irradiation of substances with radon confined to alpha-ray bulbs can be made provided the transmission of the alpha rays through the glass wall of the bulbs is known. The alpha-ray energy available after passage through the bulb is usually expressed in terms of their range in air or their total ionization in air under standard conditions. It is proposed to use here a unit which denotes the number of cubic centimeters of gas produced when the rays are absorbed by water, and in particular, to use the yield, 0.383 cc. of gas per millicurie destroyed, for 100 per cent transmission.

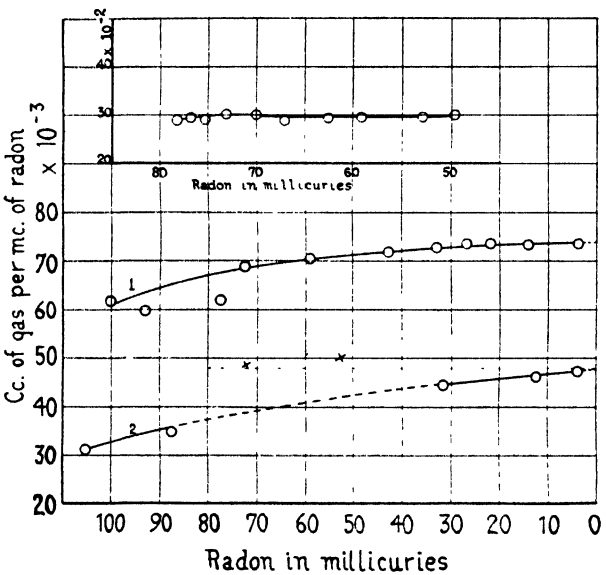

FIG. 4. CALIBRATION OF ALPHA-RAY BULBS NOS. 1 AND 2 BY THE DECOMPOSITION OF WATER

× and × indicate two experiments on ferrous sulfate

The transmissions of several alpha-ray bulbs were tested and the results of a typical experiment are recorded in the bottom half of table 1. The experimental procedure was the same as was used in the other method, except that radon was confined to the alpha-ray bulb (R, figure 1) instead of being dissolved in the water.

The method is complicated somewhat by the failure of the gas yield to follow closely the law of Cameron and Ramsay. The per cent of completed reaction ($\frac{V'}{V_\infty} \times 100$) lags behind the per cent of radon decayed as is indicated in figure 3. Furthermore, the excess hydrogen has a higher initial value and also appears to decrease more slowly than it did in the direct method.

The departure of the gas yield from the general law is demonstrated more clearly in figures 4 and 5. The gas yield per millicurie of radon is not constant, but appears to increase and approach a constant value as the quantity of radon in the bulbs decreases, or as the intensity of the rays decreases. In figure 3, curves 1 and 2 represent results with two different alpha-ray bulbs, and the difference in yields is due to differences in thickness of the bulbs. Plotted in curve 2 of figure 4 are the results of three experiments on water and two on ferrous sulfate solutions. The first experiment on water began immediately after the alpha-ray bulb had been filled with 105 mc. of radon and ended after 1 day and 27 hours. The second began after approximately 60 per cent of the radon had decayed and continued 1 day and 24 hours. The last experiment began after a new supply of radon had been added to the bulb. Between the second and third experiments, indi-

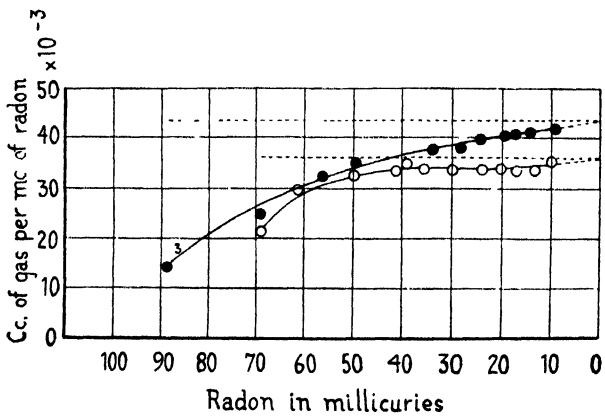

FIG. 5. CALIBRATION OF ALPHA-RAY BULB NO. 3 BY THE DECOMPOSITION OF WATER
● new bulb; ○ after the bulb had been refilled many times

cated by the dashed portion of the curve, concentrated solutions of ferrous sulfate were irradiated with the same alpha-ray bulb, and the gas yields, corrected for excess hydrogen, are indicated by the crosses. The crosses are situated above the curve such that if the gas yield from water had been constant (dotted line) with a value equal to the yield near the end of the last experiment, the crosses and the new points for water would lie approximately on the same straight line. This fact, as will be mentioned later, has an important significance in the explanation of the variation of yield with ray intensity. The top curve in figure 4 represents an experiment on the irradiation of water by the direct method. The radon in millicuries plotted as abscissas is dissolved in the water. The difference in the variation of gas yield with ray intensity for the two methods of experiment is demonstrated clearly.

In figure 5, the results of two experiments with the same alpha-ray bulb (No. 3, table 2) are shown. The agreement is fair except for the latter parts of the experiments. Here, the maximum variation is about 16 per cent, which is outside of the observational errors. The discrepancy may be due to the fact that the bulb had been filled with radon many times when the data for the lower curve was obtained. There may have been some mercury vapor or other substances condensed on the inside surface of the bulb which would give the effect of reducing the gas yield. In the course of the work it was noticed that small black deposits, probably some oxide of mercury, were visible on the bulbs. These bulbs were removed from the system and cleaned with nitric acid and water. This is a delicate process of manipulation and occasionally the bulbs were broken.

TABLE 2

Calibration of alpha-ray bulbs

BULB NO	DIAMETER	DAYS	RADON E_0	V''	PER CENT OF TOTAL TRANSMISSION	PER CENT OF ALPHA-RAY TRANSMISSION
	millimeters		*millicuries*			
1	1.8	13 8	112 5	7 708	18 6	15 3
2	2 5	1.88	105 0	1 041	8 4	4 8
		1.60	31 4	0 359	10 8	
		7 73	12 3	0 449	11 5	
		1 87*	53.1	0 773	12 4	9 0
		1.25*	72 6	0 709	12.2	8.9
3	1.8	13 9†	69 1	2 239	8 7	5 0
		10 7	91 9	3 307	10 4	7 0

* Ferrous sulfate.

† The low per cent of transmission is probably due to mercury vapor condensing on the inside wall of the alpha-ray bulb.

A summary of the results on the irradiation of water with radon in alpha-ray bulbs is given in table 2. The per cents of total transmission and alpha-ray transmission are shown in columns 6 and 7, respectively. The total radiant energy includes not only alpha rays, but also beta and gamma rays. The gamma-ray energy, however, is negligible, since the whole of it is a small per cent of the total radiant energy, and only a small part is absorbed by the water. On the other hand, an appreciable part of the gas is produced by beta rays, since practically none of them are absorbed by the glass while a large portion is absorbed by the water. From Rutherford's (17) estimation of the distribution of the total radiant energy from radium in equilibrium between alpha, beta, and gamma rays, and from the assumption that the total alpha-ray energy is divided equally between the four sources, radium,

radon, radium A, and radium C, it can be shown that approximately 4.1, 5.9, and 90.0 per cent of the total radiant energy from radon in equilibrium is possessed by the beta, gamma, and alpha rays, respectively. Since 0.383 cc. of $H_2 + O_2$ (Duane and Scheuer's value) is produced when all of the alpha rays from 1 mc. are absorbed in water, then 0.383/0.9, or 0.426 cc., is produced when all of the alpha, beta, and gamma rays are absorbed. The latter rays produce 0.025 cc., and therefore 0.401 cc. is produced by the beta and alpha rays. If this factor represents 100 per cent transmission of all beta and alpha rays through the glass wall of the alpha-ray bulbs, then a simple arithmetical calculation from the gas yields from various bulbs gives their per cent of total and their per cent of alpha-ray transmissions.

Unfortunately, the thinnest bulb, No. 1, was broken when the gaseous mixture was exploded in a second test of its wall thickness. At least six bulbs, in reaction vessels of gas volumes varying from 5 to 10 cc., and whose yields were larger than 0.06 cc. per millicurie of radon destroyed, were broken when the hydrogen and oxygen were removed by the electric spark. This yield represents a transmission of approximately 12 per cent of the alpha-ray energy, and is apparently the maximum allowable transmission without breaking the bulbs in the particular systems used in these experiments.

The experimental results lead to the conclusion that the variation of gas yield with radiation intensity is a result of the recombination of ions in the water before they become electrically neutral and pass to the gas phase. The liquid volume wherein the ions are produced is exceedingly small, and if large quantities of radon are contained in the bulbs, the ionic concentration is of the same order of magnitude as the molecular concentration of the water. The alpha-ray bulbs ranged in size from 1.5 mm. to 2.5 mm. in. diameter. The range of the alpha rays in the water is not more than a few hundredths of 1 mm. Therefore, all of the ions are produced in a thin layer of water immediately surrounding the bulbs. The idea of recombination of ions is supported by the fact that when the molecules of a concentrated solution of ferrous sulfate offer another means of escape for some of the ions, then their chances of recombination are reduced, and more become neutralized and escape to the gas phase. If, in the experiments with ferrous sulfate, an amount of oxygen equivalent to the hydrogen which is produced, is added to the hydrogen, then the new gas yield assumes a value approximately equal to the gas yield from water for the lower intensities of irradiation. This fact was mentioned previously and is indicated by the crosses in curve 2 of figure 4.

The results of Duane and Scheuer in their first experiment indicate a slight departure from the law of Cameron and Ramsay, while their second and third do not. They apparently gave no significance to it, but it is interesting to note in connection with the more marked discrepancy observed

here. In their first experiment, the capillary tube in which radon was used was approximately six times thicker than in the other two experiments. Therefore the range of the alpha particles was less, and, consequently, the region of ionization was smaller. Additional evidence that the ionic concentration may depend appreciably upon the range was observed here. One of the smallest bulbs and with the greatest wall thickness, gave results with the greatest variation from the general law.

The method of calibrating alpha-ray bulbs described in the preceding pages has some advantages over other methods commonly used. This is particularly true when the bulbs are used in systems where complete absorption is desired. Here, the calibration is determined in the chamber which is later used for other reactions. The transfer of bulbs from one system to another is eliminated. The bulbs may be filled several times with a new supply of radon, and one bulb may be used in several different experiments. The transmission is the average transmission for all parts of the bulbs, regardless of the non-uniformity of wall thickness. The thick spots at their tops and the thick portions around the steam are given their proper weight in the average value. One disadvantage is the relatively long time required for a careful determination of the transmission. The minimum time is about five days when 50 mc. of radon are used. This time, however, depends upon the capacity of the reaction chamber.

II. Oxidation of ferrous sulfate

The effects of alpha rays in solutions of ferrous sulphate in 0.8 normal sulfuric acid were studied by both the direct and indirect methods. Gas yields were determined. The procedure and the notation used in recording the results is the same as was used in the experiments on water. The solutions were stirred continuously and their temperature was kept constant. Furthermore, the quantity of ferrous sulfate changed was determined by electrometric titrations.

Three particular points of interest were investigated. It was desirable first, to study the behavior of the excess hydrogen during the course of an experiment; second, to determine the relationship between alpha-ray dosage and the per cent of ferrous sulfate changed; and third, to investigate the effects in solutions of different concentrations. These points will be discussed in the order named.

Some results of both methods are recorded in table 3. The course of the reaction is demonstrated in figures 6 and 7. The most marked difference in the gas yields from ferrous sulfate and the yields from water is the high percentage of gas left in the reaction chamber of the former when the gaseous mixture is exploded. This residual gas is assumed to be hydrogen alone; however, at the present time, no qualitative analysis of the gas has been made. If the assumption is correct, then near the end of the experi-

ment described by figure 6 the gas is almost exclusively hydrogen and in figure 7 the gas consists of nearly 97 per cent hydrogen. The action of the alpha rays on the ferrous sulfate molecules is probably a secondary effect which results from the primary decomposition of the water. The oxygen from the decomposed water is used in the oxidation of the ferrous ion, and consequently, the only gas which escapes from the liquid is hydrogen.

TABLE 3

Gas yield in the oxidation of ferrous sulfate by radon

DAYS	T_w	p_1	p_2	v_1	v_2	V	V_H	V'	PER CENT V_H	PER CENT RADON USED	$\frac{V'}{V_\infty} \times 100$
Direct method											
0 0385 molar $FeSO_4$ in 0.8 N H_2SO_4											
Solution volume = 15.0 cc.; gas volume = 4.99 cc.; initial quantity of radon = 24.4 mc.; ferrous sulfate changed = 25 per cent											
0	24 6		30 0		0.181						
0.47	24 4	88.7	87.7	0.535	0.528	0.353	0.347	0.527	98.3	8.3	9 2
1.03	24 8	128.9	127.9	0.775	0.769	0.601	0.589	0.895	98 0	17 0	15 9
2.41	24.6	255.0	255.0	1.536	1.536	1.367	1.355	2.044	99 1	35.3	35.8
3.14	24.6	301.0	300 0	1 813	1.813	1.644	1.632	2 460	99 8	43 2	43 1
4.52	24.2	376.0	377.0	2.267	2.267	2.098	2.085	3.141	99.8	55 8	55 0
5.49	23.8	424.0	424 0	2.561	2.561	2.392	2.380	3 582	99 8	62.8	62 7
7.14	24 0	485 0	485 0	2 927	2 927	2 758	2 746	4 131	99 8	72.0	72 3
Indirect method											
0.0046 molar $FeSO_4$ in 0.8 N H_2SO_4											
Solution volume = 16.0 cc.; gas volume = 9.97 cc.; initial quantity of radon 40.3 mc.; ferrous sulfate changed = 99 per cent											
0	22 2		0.1		0 007						
1.01	22.2	28.0	24.6	0.339	0.298	0.332	0.291	0.472	87.6	16.4	15 6
2.10	22.4	53.4	53.4	0 647	0 647	0 681	0.640	1.001	93.9	31.6	33.2
3 68	22.0	81.6	81.6	0 990	0 991	1 024	0.983	1.515	96.0	48 1	50.2
5.19	22.2	93 2	93.2	1.131	1.131	1.165	1.123	1.726	96.4	60.5	57.2
7.00	22 2	120 0	119.0	1.456	1.444	1 490	1.436	2.208	96.5	71 5	73.2
9.65	22.0	134 3	132.3	1 631	1.607	1.677	1.600	2.477	95.4	82.1	82.1

Here, as in the experiments on water, the law of Cameron and Ramsay applies to the gas produced, since the points representing the per cent of completed reaction follow closely the decay curve of radon.

Several samples of ferrous sulfate of the same initial concentration were exposed to different doses of alpha particle irradiation. The results of six experiments with each method are indicated by the sets of points in figures

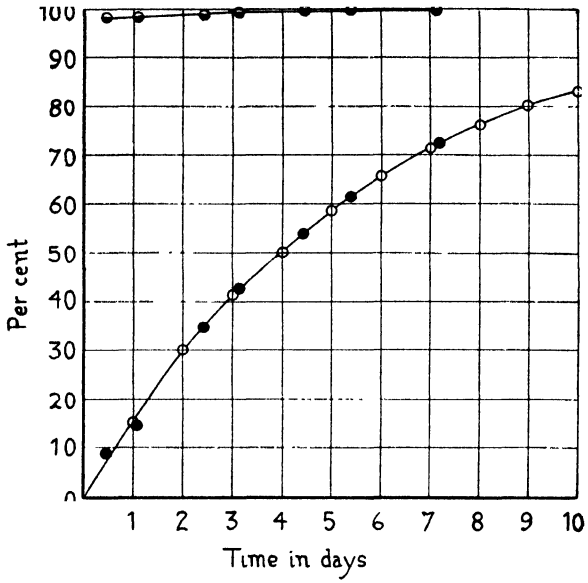

FIG 6. GAS YIELD IN THE OXIDATION OF FERROUS SULFATE BY RADON
Direct method; 0.0385 molar ferrous sulfate in 0.8 *N* sulfuric acid.
○ per cent of radon destroyed; ● per cent of completed reaction; ◒ per cent of excess hydrogen.

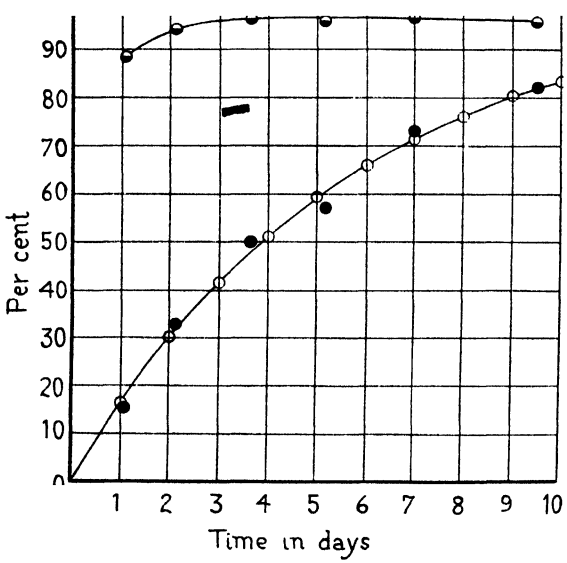

FIG. 7. GAS YIELD IN THE OXIDATION OF FERROUS SULFATE BY RADON
Indirect method; 0.0046 molar ferrous sulfate in 0.8 *N* sulfuric acid.
○ per cent of radon destroyed; ● per cent of completed reaction; ◒ per cent of excess hydrogen.

8 and 9. The liquid volumes were 20.3 cc. and 16.0 cc., and the gas volumes were 1.66 cc. and 10.0 cc. for the direct and indirect methods, respectively. The relationship between dosage and per cent of ferrous sulfate changed is linear when radon is dissolved in the solution, but when radon is in the alpha-ray bulb there is a slight deviation from the straight line. The linear relationship indicates equilibrium to be almost 100 per cent on the side of oxidation of the ferrous ion, while the curve in figure 9 may indicate some reduction of the ferric ions. The latter reaction has been observed in acid solutions (7) when irradiated with penetrating rays.

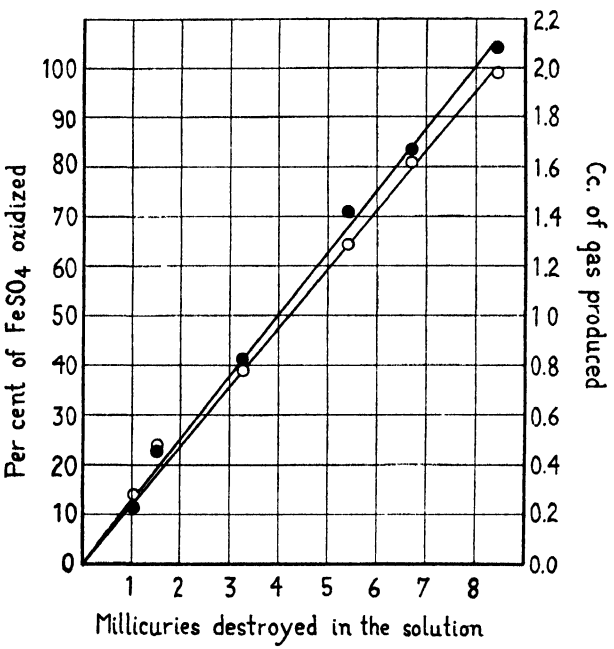

FIG. 8. OXIDATION OF FERROUS SULFATE BY RADON
Direct method; 0.0045 molar ferrous sulfate in 0.8 *N* sulfuric acid.
○ per cent of oxidation; ● gas yield.

Fricke and Morse (4) noted in one of their experiments on the irradiation of ferrous sulfate with x-rays an apparent reversal of the reaction when nearly all of the ferrous ions were oxidized. They concluded that x-rays are able to reduce the ferric ion.

The gas yields in the twelve experiments (figures 8 and 9) are indicated by the shaded circles. The separation of the lines in each figure has no significance other than its dependence upon the choice of scale. Since the gas was nearly 100 per cent hydrogen the correction due to the ionizing effects of the alpha particles in the gas is negligible. Furthermore, the quantity

of hydrogen dissolved in the solution is small and was not added to the total gas yield unless it amounted to one or more per cent of the observed hydrogen volume.

In the six experiments whose results are recorded in figure 9, the initial quantity of radon was less than 50 mc., so that, as can be seen in figure 4, the gas yield per unit of energy absorbed was more constant than it would have been for greater quantities of radon. In other words, the recombination of ions, which may occur in very dilute solutions, was reduced to a minimum.

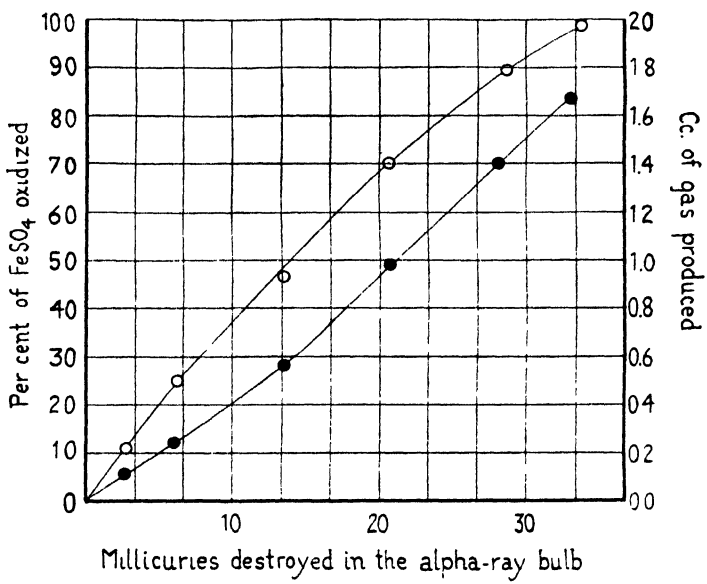

FIG. 9. OXIDATION OF FERROUS SULFATE BY RADON

Indirect method; 0.0046 molar ferrous sulfate in 0.8 N sulfuric acid.
○ per cent of oxidation; ● gas yield.

Solutions of ferrous sulfate of different concentrations were irradiated and the results are given in table 4. The concentration of each solution was determined at the beginning and the end of an experiment as described in the preceding pages. The absolute amount of ferrous sulfate transformed, expressed in milligrams per millicurie of radon decayed, is not constant, but increases as the initial concentrations of the solutions are increased from 0.00048 to 0.5 molar. This may at first seem to disagree with the results plotted in figure 7, for in figure 7 the solutions do have their ferrous ion concentration reduced; however, the yield per millicurie remains constant. Close inspection of table 4, however, shows that the numerical values in column 4 seem to approach a constant value as the solution con-

centration is reduced; and furthermore, the range of concentrations in the experiments of figure 8 is either equal to or less than the minimum concentration of table 4. The irradiation of solutions of initial concentrations less than 0.00048 molar might have added more information in regard to this point; however, they are difficult to study, since small quantities of radon produce large percentages of transformation. Consequently, the end point of the titration curve is not distinct. Moreover, the gas yield is too small to measure accurately with the apparatus employed.

The chemical action of the alpha rays in the ferrous sulfate solutions is expressed in terms of the ionization of the rays in the last two columns of

TABLE 4

Oxidation of ferrous sulfate by radon in solutions of different concentrations

CONCENTRATION	PER CENT OXIDIZED	RADON USED	MILLIGRAMS CHANGED PER MC. OF RADON	VOLUME OF H_2	PER CENT OF H_2	$\frac{M\ FeSO_4}{N}$	$\frac{M_{H_2}}{N}$
			Direct method				
molar		*millicuries*					
0.5000	2.3	8.04	12.4	2.067	99.2	3.13	0.80
0.0498	30.4	12.5	5.52	3.342	99.5	1.40	0.83
0.0333	7.2	5.90	4.01	1.438	94.2	1.01	0.74
0.0045	39.6	3.33	3.02	0.947	94.7	0.78	0.88
			Indirect method				
0.4100	4.4	15.2	3.80	0.534	100.0	8.10	0.91
0.0460	12.8	14.9	1.27	0.762	94.5	2.75	1.32
0.0046*	37.4	6.87	0.81	0.372	95.9	1.70	1.41
0.0045†	37.4	10.6	0.75	0.500	92.0	1.68	1.33
0.00048	57.9	1.33	0.70	0.095	78.0	1.64	1.85

* Alpha-ray bulb No. 2.
† Alpha-ray bulb No. 3.

table 4. M_{FeSO_4} denotes the number of ferrous sulfate molecules transformed and is equal to $\frac{m \times 6.06 \times 10^{23}}{277.9 \times 1000}$, where m denotes ferrous sulfate transformed in milligrams, 6.06×10^{23} is Avogadro's number, and 277.9 is the molecular weight of $FeSO_4 \cdot 7H_2O$. N denotes the number of ion pairs formed in water by the absorption of a quantity of radiant energy equal to that absorbed by the solutions. The factors in the calculation of N were described previously. The ratio M_{FeSO_4}/N in both methods decreases with concentration, but not linearly. It seems to approach a constant value for dilute solutions. The number of molecules of hydrogen which are produced per ion pair is expressed by the ratio M_{H_2}/N. The

ratios, M_{FeSO_4}/N and M_{H_2}/N, are in most cases nearly 50 per cent greater in the indirect method than in the direct method. It was at first thought that the difference in yields might be partially due to errors in the determination of the transmission of the alpha-ray bulb. However, the results obtained with two different bulbs (Nos. 2 and 3, table 2) agree and so it is unlikely that the M/N values of the two methods differ owing to errors in transmission determinations.

DISCUSSION OF RESULTS

The increase of M_{FeSO_4}/N without a corresponding increase of M_{H_2}/N when solutions of greater concentrations of ferrous sulfate are used complicates the reaction beyond expectation. When the work began, it was thought that the reaction would most likely be a simple oxidation of the ferrous ions to ferric ions by the oxygen of the decomposed water. If the activated water molecules or the ions resulting from the dissociation of the water molecules simply oxidized the ferrous ion and no other reaction is present, then M_{H_2}/N would be some constant multiple, most likely two, of M_{FeSO_4}/N; that is, M_{FeSO_4}/M_{H_2} would be equal to 2. The experimental results do not verify this conclusion, and, therefore, other reactions must be present. Whatever the side reactions may be, they must proceed with the oxidation of ferrous ions without liberating hydrogen. Chemical analyses of the reaction products have not as yet been studied and therefore no definite statement about their nature can be made. It is interesting to note that if there be added to M_{H_2} (table 4) the number of molecules of oxygen contained in a volume equivalent to the hydrogen volume, then $\frac{M_{H_2} + M_{O_2}}{N}$ would have a value near to that for pure water.

Fricke and Morse (9) irradiated aqueous solutions of ferrous sulfate in 0.8 N sulfuric acid with x-rays from a water-cooled tungsten tube. They obtained for solutions whose concentrations varied from 0.00878 to 0.0000406 gram-molecules in 1000 g. of solution, a linear relationship between the x-ray dosage and the per cent of ferrous sulfate transformed up to the arbitrary dose 29. Beyond 29, the relation is linear, but the line describing it has a different slope. They attribute the sharp break in their curve as occurring when all of the dissolved oxygen in the solution is consumed. Moreover, they find that M_{FeSO_4}/N, where M_{FeSO_4} has the same meaning as is defined in the preceding pages, and N is the number of ion pairs formed in air by the absorption of the same amount of x-rays as is absorbed in their solutions, is equal to 5.7 when the solution contains oxygen and is equal to 2.8 when the solution does not contain oxygen. These values are within the range of variation of M_{FeSO_4}/N given in table 4. However, the latter are obtained after the dissolved gases in the solution were partially removed, and, therefore, the higher yields cannot be

attributed to dissolved oxygen alone. Furthermore it is difficult to understand why the consumption of oxygen should end so suddenly as is indicated by the sharp break in the slope of their curves.

SUMMARY

1. Two methods, called the direct and indirect, of irradiating liquids with alpha-rays from radon are described, and the errors and their corrections in the direct method are discussed.

2. The decomposition of water by alpha rays is suggested as a method for the determination of the transmission of alpha-ray bulbs. The gas yields are shown to deviate somewhat, owing to recombination of ions in the water, from the general law of Cameron and Ramsay.

3. Aqueous solutions of ferrous sulfate were irradiated by both methods. The gas yield is nearly 100 per cent hydrogen. Equilibrium lies almost 100 per cent on the side of oxidation of the ferrous ions to ferric ions.

4. Milligrams of ferrous sulfate changed per millicurie of radon destroyed increase when the initial concentration of ferrous sulfate is increased from 0.00048 molar to 0.5000 molar.

5. The ratios M_{FeSO_4}/N and M_{H_2}/N vary with the concentration of ferrous sulfate. Furthermore, M_{FeSO_4}/M_{H_2} is not equal to two and therefore reactions other than the oxidation of the ferrous ions by the decomposition products of water are present.

6. Dissolved oxygen alone does not account for the yield of oxidized ferrous sulfate.

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THE EFFECT OF ULTRA-VIOLET RAYS ON THE ULTRA-VIOLET ABSORPTION SPECTRUM OF AQUEOUS METHYLENE BLUE SOLUTIONS

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In 1912 Lasareff (7) observed that methylene blue was bleached by sunlight if it were spread on thin plates in the form of a gelatin solution. The bleaching of the visible spectrum of methylene blue has been reported also by Gebhard (1) and Krestownikoff (6). Iimori and Kitaoka (4) found that methylene blue was decolorized by exposure to the rays of the mercury arc. Hill (3) has used the fading of solutions of methylene blue in 30 per cent acetone to measure the ultra-violet intensity in the "physiologically active" region of the spectrum. Stenström and Lohmann (9), in an investigation of the fading action of Roentgen rays on various colored solutions, found that aqueous methylene blue solutions were faded by the rays. In this paper we shall report the changes in the ultra-violet absorption spectrum of aqueous methylene blue solutions following irradiation with ultra-violet rays.

The accurate determination of absorption bands by the visual selection of points of equal density on a photographic plate is made more difficult by the uncontrollable variations in the intensity of the light source. Some of the errors of this method are eliminated by the use of the Judd Lewis (8) sector photometer, manufactured by Adam Hilger, London, since, by the use of this instrument, simultaneous and adjacent spectra of the light passing through both photometer and solution are obtained.

In this laboratory, we use an under-water tungsten spark of the type recommended by the Bureau of Standards (2) as a source of light. The advantage of such a source lies in the fact that the resulting spectrum is continuous and relatively free from intense emission lines. Light from this source is split by the lens system of the apparatus into two parallel beams. The upper of the two beams passes through the solution whose absorption bands are being determined, while the lower one passes through a variable sector photometer and, if it is desired, through the pure solvent used in making the solution. (We have always taken the precaution of placing either the pure solvent or distilled water in the lower beam.) The two beams pass through the lens system of a quartz spectrograph and are

then brought together on a photographic plate, the image of the upper one lying just above that of the lower. The light source previously has been carefully adjusted so that the two images are equally intense when the photometer is opened completely and when no solution is placed in either beam. A series of photographs is then made on one plate. The customary method is to take the first exposure with the photometer set at 0.1 (on the lower of the two photometer scales), the second exposure with the photometer set at 0.2, and so on, the last exposure being made when the photometer is set at 1.5. In order to keep constant the density of the spectrum on the photographic plate produced by the light passing through the sectors, it is necessary to use a different time of exposure for each sector setting. The time of each exposure is calculated conveniently by means of the formula,

$$\text{Exposure time} = A\,\frac{J'}{J}$$

where A is a constant and where J'/J is the ratio of the light intensity before the light enters the photometer to that after it has passed through the photometer. The constant, A, is easily determined by experiment. The ratio, J'/J, is the antilogarithm of the lower scale reading of the photometer scale. After the plate is developed (which process requires no special care, since the pairs of spectra are both exposed and developed simultaneously and under identical conditions), the points of equal density on each of the pairs of spectra are determined by using a suitable ocular and are marked with India ink. The extinction coefficients (5) can then be calculated by means of the relation,

$$K = \frac{1}{L}\log_{10}\frac{J'}{J}$$

where K is the extinction coefficient, L is the length (in centimeters) of the absorption chamber used, and $\log_{10} J'/J$ (slight corrections, found in the directions furnished by Hilger, must be applied), the logarithm of the ratio of the light intensity before the beam enters the photometer to that after it leaves it, is the lower reading of the photometer scale. A wave length scale is provided with the spectrograph; two images, one at the bottom and one at the top of the series of exposures, are recorded on the photographic plate by means of 15-second exposures with a 40-watt electric lamp. The wave length corresponding to each India ink dot is determined by placing a straight edge across the two wave length scales and moving it until the edge passes through the center of the dot. By plotting the extinction coefficient as a function of the wave length, the absorption bands can be illustrated in graphic form.

EXPERIMENTAL

A standard solution of methylene blue, containing 0.1 mg. of dye per cubic centimeter was made by dissolving recrystallized methylene blue in distilled water. From this stock solution, working solutions were prepared by dilution. By preliminary experiments, it was found that 0.008 mg. per cubic centimeter represented the correct concentration to show photographically the ultra-violet absorption bands when a 2-cm. absorption chamber was used. Accordingly this concentration was used in all our experiments.

As a source of ultra-violet light for the irradiation of the methylene blue solutions, we used a Victor mercury arc lamp. All the solutions irradiated were placed at a distance of 30 cm. from the center of the lamp bulb. The

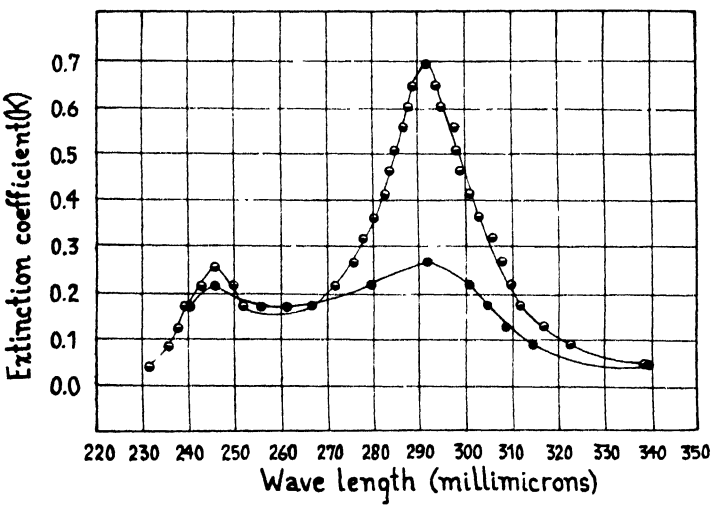

FIG. 1. ULTRA-VIOLET ABSORPTION SPECTRA OF METHYLENE BLUE IN DISTILLED WATER

⊖ before irradiation; ● after irradiation

operating voltage of the lamp varied between 65 and 70 volts. In all cases except one (where distilled water was used as the solvent) the time of exposure was 2 hours.

Figure 1 shows the absorption curve of methylene blue in distilled water, both before and after irradiation. A 20-cc. sample of the solution was placed in a small Petri dish (forming a layer of solution 0.8 cm. thick) and exposed to the rays. After a period of one hour, fading had become so marked that irradiation was stopped. The ultra-violet absorption curve shows that a very definite decrease in absorption had occurred in the ultra-violet region of the spectrum. The transmission at 670 millimicrons (point of maximum absorption of visible light by methylene blue (9)), as

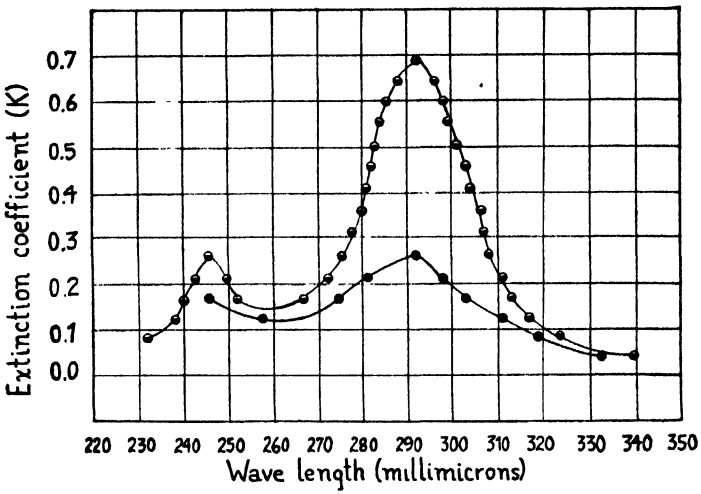

FIG. 2. ULTRA-VIOLET ABSORPTION SPECTRA OF METHYLENE BLUE IN HYDROCHLORIC ACID–POTASSIUM CHLORIDE SOLUTION (pH 2.19)

◓ before irradiation; ● after irradiation through quartz

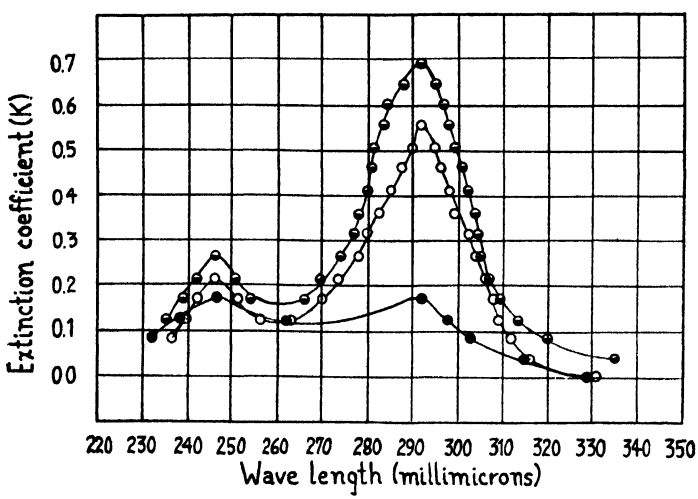

FIG. 3. ULTRA-VIOLET ABSORPTION SPECTRA OF METHYLENE BLUE IN PHOSPHATE SOLUTIONS (pH 6.69)

◓ before irradiation; ● after irradiation through quartz filter; ○ after irradiation through Blue-purple Corex A filter.

determined by a Bausch and Lomb spectrophotometer, increased from 0.0008 to 0.478 as a result of the irradiation.

In order to be sure that the observed fading was caused by the ultra-

violet rays and not by the heat produced by the lamp, two experiments were performed. Some of the same solution used above was irradiated under conditions identical with those described, except that it was protected by a thin sheet of ordinary window glass. No change in either visible or ultra-violet regions of the spectrum occurred. In addition, some of the same solution was boiled for several minutes, the beaker being covered with a

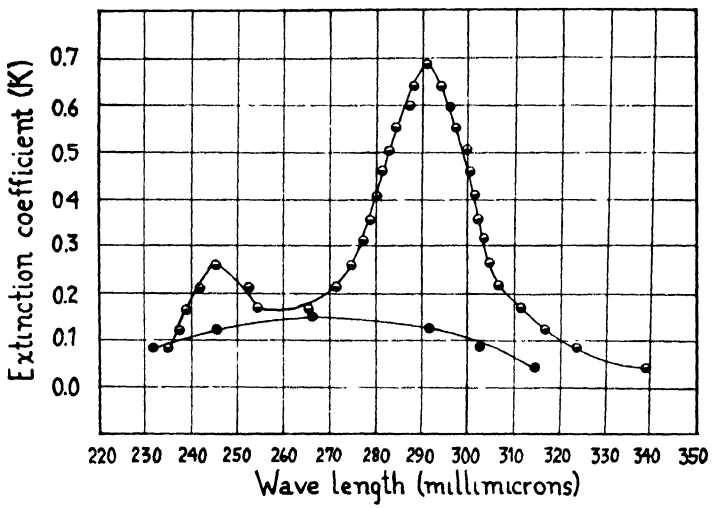

FIG. 4. ULTRA-VIOLET ABSORPTION SPECTRA OF METHYLENE BLUE IN SODIUM BORATE SOLUTION (pH 9.08)

◒ before irradiation; ● after irradiation through quartz filter

TABLE 1

SOLVENT	FILTER	pH		J J′ (670 MILLIMICRONS)	
		Before irradiation	After irradiation	Before irradiation	After irradiation
HCl–KCl buffer	Quartz	2 19	2 18	0 0007	0 125
Sodium borate buffer	Quartz	9 08	9 07	0 0008	0 699
Phosphate buffer	Quartz	6 69	6 68	0 0008	0 660
Phosphate buffer	Blue-purple Corex A	6 69	6 70	0 0008	0 005

watch glass to prevent evaporation. In this case, also, the methylene blue spectrum was not altered.

The work of Stenström and Lohmann (10) has brought out the fact that pH apparently has little or no effect on the visible absorption spectrum of methylene blue solutions before exposure to Roentgen rays, but that during exposure greatest fading takes place in solutions of highest pH. Our ex-

periments have shown this to be true also in the case of ultra-violet irradiation. The effect of pH is illustrated by figures 2, 3, and 4 and by table 1. The pH of the solutions was measured potentiometrically.

In an attempt to determine which wave lengths were most effective, several filters—including window glass, Vita glass, Clear Corex D, Blue-purple Corex A, and quartz—were used. In the case of all the filters except quartz, the following procedure was adopted: 20c c. of the methylene blue solution was placed in a small Petri dish, after which the dish was covered with the filter. Irradiation was carried out as described above. In order to eliminate any possible effects due to ozone formation, irradiations in which the quartz filter was used were carried out by placing the

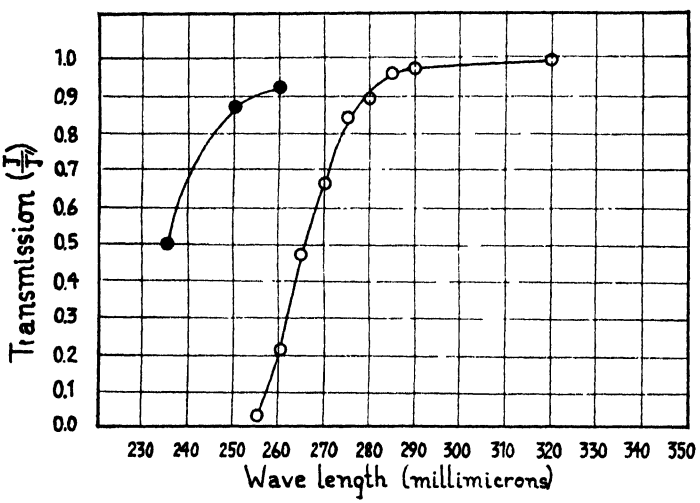

FIG. 5. ULTRA-VIOLET TRANSMISSION CURVES FOR FILTERS
● quartz; ○ Blue-purple Corex A

solution in a small, completely closed quartz vessel. Ultra-violet transmission curves of the filters were determined by means of a quartz spectrograph in combination with a microphotometer. The curves for the particular samples of Blue-purple Corex A and quartz used are given in figure 5. The transmission curve for the quartz was taken through the quartz vessel mentioned above and represents, therefore, the transmission of a filter of twice the thickness actually used. Figure 4 and table 1 show that the decrease in absorption produced when the Blue-purple Corex A filter was used was slight as compared with that produced with the quartz filter. Since the transmissions of the other filters were less than that of the Blue-purple Corex A glass, their transmission curves are not included here. It appears that the wave lengths most active in decreasing the absorption bands of methylene blue are shorter than 270 millimicrons. For this

reason we do not believe that the change in aqueous solutions of methylene blue produced by ultra-violet rays can be used for the purpose of measuring the radiation intensity between 290 and 310 millimicrons (the "physiologically active" region of the spectrum).

SUMMARY

1. The method of using the Judd Lewis sector photometer in combination with the quartz spectrograph is briefly described.

2. The ultra-violet spectrum of methylene blue is included. Maximum absorption occurs at 292 millimicrons and at 246 millimicrons.

3. Exposure of methylene blue solutions to ultra-violet rays causes a decrease in the absorption bands in both visible and ultra-violet regions of the spectrum.

4. pH has no effect on the ultra-violet spectrum of methylene blue solutions, but irradiation with ultra-violet light causes greatest change in solutions which have highest pH.

5. The wave lengths most active in decreasing the absorption bands of methylene blue solutions are shorter than 270 millimicrons.

The authors wish to express their gratitude to Dr. W. K. Stenström who suggested the problem and whose cooperation has made this investigation possible.

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AN APPROACH TO AN EXPLANATION OF THE SURFACE WORK FUNCTIONS OF PURE METALS

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Up to six or seven years ago the developments in the field of metal surface work functions had resulted in the recognition of the following principles (2, 4, 5, 8, 9):

1. Each metal has an intrinsic potential that is characteristic of the pure metal. (These characteristic potentials are the origins of the volta effect, the photoelectric effect, thormionic emission, and electromotive force.)

2. A characteristic potential can be represented diagrammatically as a surface barrier, or a condenser on the surface of the metal.

3. Part of each barrier is the work performed by an emitted electron against the attraction of the electric image.

4. Emitted electrons are subject to the image forces only when they are outside of a distance which is characteristic of the metal.

These are the older principles that are very useful at the present time.

In the last seven years there has been developed a concept of metals which is based on the behavior of the electrons in metals according to the Pauli exclusion principle, with the valence electrons exhibiting the Fermi-Dirac distribution of velocities. As a result of the great and increasing usefulness of this new theory, several additional principles concerning electron emission must be recognized (6, 7, 10).

1. If there are a number of free electrons comparable to the number of atoms in a metal, then the electrons will obey the Fermi statistics and behave as a degenerate gas. (All of the distinctly metallic substances fall in this category.)

2. The electrons on the interior of metals are credited with possessing considerable kinetic energy even at absolute zero. (The energies are as great as from 5 volts to 15 volts.)

3. The total surface barrier must be four or five times the net or external surface work function. The net surface work function is just the difference between the total surface work function, W_a, and the maximum kinetic energy of the electrons, which is equal to U_0 at 0°K.

In its gross outline the problem which the author is attacking is the explanation of the existence of the total surface work function, W_a, which

serves as a barrier to the escape of the electrons of a metal. Using the above principles and the results of the work of Bartlett and Waterman, a simple analysis shows that the total barrier of pure metals is made up of three parts (figure 1): (1) the space charge potential energy, (2) the image potential energy, and (3) the potential energy due to the different initial and final electrostatic environments.

The first of these divisions has been treated by Bartlett and Waterman (1, 13). The results of their calculations show that "space charge" effects will account for the reduction of the kinetic energy of the electrons from their enormous Fermi energies to their classical $(3/2)kT$ energy. Or, giving a probable broad meaning to these results, a "space charge" barrier surrounds a metal surface to the extent that this part of the barrier contributes nothing to the net surface work function but merely balances the

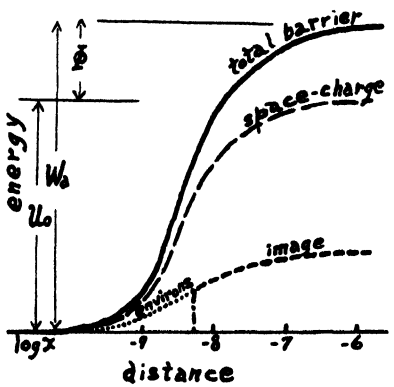

FIG. 1

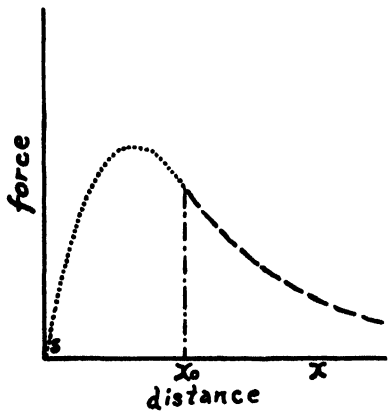

FIG. 2

0°K. kinetic energy of the electrons, so that without the existence of the other two divisions of the barrier it would be possible to draw electrons out of metals using only slight external fields under any condition of temperature or radiation.

The second of these divisions is well understood from the standpoint of classical electrostatics. Its nature is such that it must be included in the net work function part of the total barrier. The problem involved in understanding the image forces is only the determination of how close to the metal surface they are effective. It has been popular in the past to consider this problem along with those connected with the third division of the barrier, and this treatment has been found quite effective by the author.

The above discussion of the first two divisions of the barrier concentrates the burden of the explanation of metal surface work functions on to the solution of the problem concerning the third division, the work done by

the electrons in emerging far enough from their local electrostatic environment so that the image furnishes the environment. Consequently the main discussion of this paper suggests a hypothesis to serve as a basis for this division of the potential barrier.

The most acceptable classical approach to an understanding of metal surface work functions is the Langmuir modification of the Schottky principle (5). According to this theory the change in the force acting on an electron is proportional to the displacement of the electron from its initial equilibrium position. At a distance x_0 (figure 2) the parabolic force–distance curve merges into the hyperbolic force–distance curve of the image forces. The surface work function is inversely proportional to this distance x_0. This modification of Langmuir's is arbitrary because the postulations of other shapes for the curve inside distance x_0 will account for some of the phenomena of surfaces to the same extent. However the general shape of this curve is admitted to be quite logical in terms of our present knowledge of cohesive and repulsive forces. It might be pointed out also that the equation which the author will use later could serve as a first approximation of some more complicated functional relationship.

All of the theories have stalled at this point. Distance x_0 was identified with the distance between the ions in the crystal, which varied considerably with the temperature. Φ is inversely proportional to x_0; consequently Φ should vary considerably with the change in temperature. This is not so. The photoelectric threshold of a metal not only changes very slightly with change in temperature but its change is quantitatively predicted by Fowler's theory, which is based on the change in the kinetic energy of the electrons in the metal at elevated temperatures in accordance with the Sommerfeld theory of metals. Necessarily the correct hypothesis to explain the net work function must account for its being independent of the temperature, aside from its change predicted by the Maxwell-distribution-law tail to the Fermi-Dirac distribution of the electron velocities in metals.

The following principles are used by the author as guides for his approach to an explanation of the net work function: (1) The electrons should be considered as more or less in condition of equilibrium in a field of force characteristic of the crystal. (2) The Langmuir modification of the Schottky principle should be useful providing x_0 is identified with some quantity other than the distance between the atoms. (3) The net work functions should be independent of the temperature. (4) The hypothesis should allow the calculation of the Φ's for the various metals.

A study of these principles leads to this hypothesis. *The slope of the force–distance parabola is identified with the lattice energy of the metal crystal and can be assumed to be equal to a constant times the electrostatic potential energy of the crystal.*

There are two sources from which one can obtain the values of the

electrostatic potential energy constants for metals. One source requires the complete knowledge of the crystal structure of the metals and involves lengthy calculations. The other source is readily available and the calculations are very simple, although indirect. These calculations involve starting from the compressibilities of the metals, using the principles developed by J. J. Thomson (12), and calculating the linear potential energy constants of the various metals.

If

$$K \text{ (the bulk modulus of compressibility)} = C\left(\frac{\Delta}{M}\right)^{4/3}$$

$$P \text{ (the potential energy constant)} = \frac{C}{4.5}\left(\frac{\Delta}{M}\right)^{1/3}$$

or

$$P = k'''' K \frac{M}{\Delta}$$

The formula for the parabola in the force–distance curve is

$$y = \frac{k'x}{x_0^3} - \frac{k''x^2}{x_0^4}$$

When $x = 0$,

$$S = \frac{dy}{dx} = k' \frac{1}{x_0^3}$$

or

$$x_0 = \frac{k'''}{S^{1/3}}$$

Since

$$S = c'P$$

and also

$$\Phi = \frac{c''}{x_0}$$

then

$$\Phi = c'''\left(\frac{KM}{\Delta}\right)^{1/3}$$

(The k's and c's are constants)

Using the last equation the author has calculated the values of the intrinsic potentials of a large number of metals. The value of the constant

was evaluated from the experimental values of the potentials. The values of the compressibilities and densities were taken from the International Critical Tables. With one exception the largest of the accepted values for compressibilities of metals was used. The calculated values are com-

TABLE 1

METALS USED FOR COMPARISON	CALCULATED VALUES (J.F.C.)	ARBITRARY EXPERIMENTAL VALUES	VALUES ACCEPTED AS GOOD	HENNING CONTACT POTENTIALS	RICHARDSON PHOTO-ELECTRIC THRESHOLD	MISCELLANEOUS		
						Photo-electric*	Photo-electric*	Thermionic values†
K	2 06	1 99* (Iv)‡				1 99 (Iv) 2 1 (S)	1 9 (Ho) 2 2 (Ol)	
Na	2 11	2 1* (Ri)			2 1	2 2 (P & P)	1 8 (Mi)	
Li	2 07	2 2* (Mi)				2 3 (Ol)	2 2 (Mi)	
Ca	3 00	3 0* (Ri)			3 0	2 8 (We)	3 08 (Ha)	
Mg	3 11	3 2* (Ri)		2 63	3 2			
Al	3 58	3 57* (R)	3 57	3 06	2 8	3 57 (R)	3 4 (H & K)	
Zn.	3 64*	3 68* (R)	3 5	3 46	3 4	3 68 (R)	3 57 (D)	
Sn	3 86	3 78c (H)	4 50 4 38	3 78	3 5	4 38 (G)	4 50 (G)	
Cu	3 88	3 85* (W & S)	4 38		4 1	3 85 (W & S)	4 1 (H & K)	4 38 (G)
Fe	4 18	4 2* (R)	4 72	3 86		4 2 (R)	4 72 (C) 4 1 (H & K)	
Co	4 20	4 25† (C)	4 25 4 12			4 0 We		4 25 (C) 4 12 (C)
Ni	4 22	4 12* (R)	5 01			4 12 (R) 5 01 (G)	4 1 (Ha) 4 1 (We)	
Ag	4 33	4 30* (S)	4 68 4 56	4 05		4 30 (S) 3 85 (R)	3 8 (Wer) 4 58 (Wi)	4 08 (G)
Pd	4 67	4 96*† (DB)	4 96			4 4 (Wer)	4 96 (DB)	4 99 (DB)
Au	4 71	4 72* (Mo)	4 72			4 72 (Mo)	4 82 (Mo)	4 42 (G)
Mo	5 02	4 41† (D)	4 41			4 33 (R)	3 22 (Ma)	4 41 (D) 3 48 (Ma)
Ta	5 00	4 07† (D)	4 07 4 05			3 92 (R)	4 05 (C)	4 07 (D) 4 31 (L)
Pt	5 34	5 45* (W)	6 30		4 3	4 40 (R) 4 62 (S)	6 30 (DB)	6 27 (DB)
W	5 67	5 45* (Hag)	4 52			4 52 (R) 4 58 (Wer) 5 4 (Hag)	4 80 (Wer) 4 50 (D & G)	4 52 (L) 4 52 (D)

* See columns 3, 7, and 8

† See columns 3 and 9

‡ C = Cardwell, D = Dushman; DB = DuBridge, G = Goetz, H & K = Henning and Kadesch, H = Hennings, Ha = Hammer; Hag = Hagenow, Ho = Hamleck; Iv = Ives, L = Langmuir, Mi = Millikan; Ma = Martin, Mo = Morris, Ol = Olpin; P & P = Pohl and Pringlheim, R = Roy, Ri = Richardson, S = Suhrman; We = Welch, Wi = Winch; Wer = Warner.

pared with the arbitrary experimental values which were used to evaluate the constant and other values which were largely taken from a collection made by Hughes and DuBridge (3) in table 1.

A careful study of the table will show any one familiar with the field that the agreement between the calculated and the experimental values

is better than the experimental results demand in order to show the probable validity of the relationships. In fact the agreement between the calculated values and the experimental values obtained when the best of outgassed conditions were not present is nothing short of remarkable. The author's equation predicts that Φ is practically independent of the temperature. K/Δ shows very little variation with the variation of the temperature; the value of K/Δ is greater than one; consequently the cube root of K/Δ is practically independent of the temperature. The useful (useful when applied to pure metals) Schottky principle is maintained intact. In addition the requirement of Tamm and Schubin (11) is met. In short, the author's theory with its subordinate hypotheses seems to be a tool of considerable usefulness.

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RHYTHMIC PRECIPITATION WITH ORGANIC PRECIPITANTS[1]

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As a result of many investigations (6) since Liesegang's discovery (8) of rhythmic precipitation there is considerable belief (1, 2, 7, 9) that it is a general phenomenon and may occur under suitable conditions with any pair of substances that form a fairly insoluble precipitate.

When precipitation occurs in gels Hedges (5) distinguishes four types of structures that may appear: (a) precipitates of continuous structure very finely divided, as with silver chloride; (b) discrete structures frequently containing well-formed crystals of significant size; (c) cellular structures; and (d) periodic structures with definite bands or rings. In view of these different possibilities it seemed of interest to determine the type of structure produced in a gel by precipitates formed with certain organic compounds that are finding increasing use in analytical chemistry. Precipitates such as nickel dimethylglyoxime are very voluminous in character.

EXPERIMENTAL WORK

Materials

Gels of silicic acid or agar were used, the former being prepared from sodium silicate and the latter from an American product. Salts were of "reagent" quality and organic compounds were used as purchased.

Procedure

As preliminary experiments showed that solutions of the organic precipitants did not diffuse well into the gels, in most cases these compounds were put in the gels and the solutions of the salts on top. Agar gels were prepared by dissolving 1 g. of agar in about 80 ml. of hot water, adding 10–20 ml. of a solution of the organic compound, diluting the mixture to 100 g., and filtering through glass wool into test tubes which had been previously coated with gelatin (3) to assist the gel in sticking to the tube. In preparing gels of silicic acid, sodium silicate was dissolved in water to give a solution of approximately 1.06 specific gravity. The alkalinity of the

[1] Taken from Part I of a dissertation presented by J. E. Heck to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

TABLE 1

Data for silica gels

GEL						DIFFUSING SOLUTION		STRUCTURE
Precipitant			Sodium silicate		Reaction	Salt	Concentration	
Material	Volume	Concentration	Volume	Specific gravity				
	ml.		*ml.*					
1*	13.0	Satd. soln. 0.96 *N* AcOH	8 0	1 06	b†	$CuSO_4$	1.0 *N*	GB
1	14.0	"	8.0	1 06	a	"	1.0 *N*	FB (364)
1	13.0	"	8.0	1 06	b	$Cu(NH_3)_4SO_4$	1.0 *N*	FB
1	14.5	"	8 0	1.06	a	"	1.0 *N*	FB
2, 4	10.6	"	10.0	1.08	a	$CuSO_4$	1.0 *N*	PB, PB
2, 4	14.8	"	8.0	1 06	a	$FeCl_3$	1.0 *N*	PB, NP
2	14.8	"	8.0	1.06	a	$CuSO_4$—20 ml. AcONa—1 g.	1.0 *N*	PB
3	10.0	"	10 0	1 08	a	$Ni(NO_3)_2$	1.0 *N*	NP
3	13.6	"	8.0	1.06	b	$CuSO_4$	1.0 *N*	PB
3	13.6	"	8 0	1.06	b	KOH—2 drops $Cu(NH_3)_4SO_4$	10 per cent 1.0 *N*	DS
3	10.0	"	10.0	1 08	a	"	1.0 *N*	DS
3	13.6	"	8.0	1.06	b	KOH—2 drops NH_4Cl—3 ml. $Ni(NH_3)_4(NO_3)_2$	10 per cent 10 per cent 1 0 *N*	DS
3	10.0	"	10.0	1.08	a	KOH—2 drops $Ni(NH_3)_4(NO_3)_2$	10 per cent 1.0 *N*	NP
4, 8	10.6	"	10.0	1.08	a	$CoCl_2$	1.0 *N*	NP, CS
4, 8	14.8	"	8 0	1.06	a	"	1.0 *N*	NP, FB
5	10.3	2.5 g. per liter 0.97 *N* AcOH	10.0	1.08	a	$ZnSO_4$	1.0 *N*	PB
5	10.3	"	10.0	1 08	a	$CdSO_4$	Saturated	CS
5	11.3	"	10.0	1 08	a	"	1.0 *N*	PB
5	11.3	"	10.0	1.08	a	$CuSO_4$	1.0 *N*	PB
5	12.3	"	10.0	1 08	a	$Al_2(SO_4)_3$	1 0 *N*	PB
6	13.0	6.0 g. per liter 0.96 *N* AcOH	10 0	1 08	a	KNO_3	1.0 *N*	F (344)
6	16.0	3.0 g. per liter 0.96 *N* AcOH	8.0	1 06	a	"	1 0 *N*	F (347)
6	11 0	"	10 0	1 08	a	"	1.0 *N*	F (351)
7	9.6	Satd. soln. 0.96 *N* AcOH	10 0	1 08	n	$CoCl_2$	1.0 *N*	PB

* In the column headed "Material" the numbers refer to the following precipitants: 1, α-benzoin oxime; 2, cupferron, 3, dicyandiamidine sulfate; 4, dinitrosoresorcinol; 5, 8-hydroxyquinoline; 6, nitron; 7, nitroso-β-naphthol; and 8, phenylthiohydantoic acid.

† The reaction of the gels is indicated as follows: a, acidic, b, basic, and n, neutral.

TABLE 1—*Concluded*

GEL						DIFFUSING SOLUTION		STRUCTURE
Precipitant			Sodium silicate		Reaction	Salt	Concentration	
Material	Volume	Concentration	Volume	Specific gravity				
	ml.		*ml.*					
7	10 6	Satd. soln. 0 96 *N* AcOH	10.0	1 08	a	$CoCl_2$	Saturated	CS
7	9.6	"	10 0	1.08	n	H_2O_2—15 ml. $COCl_2$—50 ml.	3 per cent 1.0 *N*	FB
7	10.6	"	10 0	1 08	a	"	3 per cent Saturated	CS
7	10.6	"	10 0	1.08	a	$FeCl_3$	1 0 *N*	CS
8	10.6	"	10 0	1.08	a	$CdSO_4$	1 0 *N*	PB
8	10 6	"	10 0	1 08	a	$HgCl_2$	Saturated	GB (335)
8	13 8	"	8.0	1.06	n	"	"	FB
8	13 8	"	8 0	1.06	n	$CoCl_2$	1.0 *N*	FB
8	13 0	"	8 0	1 06	b	"	Saturated	FB
8	14.0	"	8 0	1.06	a	"	"	FB
8	13.8	"	8 0	1 06	n	$CdSO_4$	1 0 *N*	FB
8	14 8	"	8 0	1 06	a	$Pb(NO_3)_2$	1 0 *N*	CS
8	13 0	"	8 0	1 06	b	"	Saturated	PB
8	14.0	"	8 0	1 06	a	"	"	PB
8	13.0	"	8 0	1 06	b	$CuSO_4$	"	GB (353)
8	15 0	"	8 0	1 06	a	"	1.0 *N*	PB

solution was determined by titration with an acid, using phenolphthalein as the indicator. Based on this, acetic acid containing the precipitant was added to give an acidic, neutral, or basic gel, as indicated in table 1. After the gels set (within an hour) normal or saturated solutions of the different salts were placed over them in the tubes. For each mixture three tubes were prepared, one of which was kept in the dark in order to determine the effect of light on the formation of the precipitates.

Data

Tables 1 and 2 give the composition of the different gels and the diffusing solutions, together with an indication of the types of precipitation observed. Figures 1 to 4 show the characteristics of some of the more striking structures. The types formed are indicated in the tables as follows: GB, good bands; FB, fair bands; PB, poor bands; CS, continuous structure; DS, discrete structure; F, fern-like structure; and NP, no precipitate.

For the tubes shown in figure 1 certain variations were made so that they are considered separately. The gel in tube 14 was basic, being made from sodium silicate, hydrochloric acid, and alcoholic dimethylglyoxime. The

TABLE 2

Data for agar gels

PRECIPITANT IN GEL		DIFFUSING SOLUTION		STRUCTURE
Material	Concentration	Concentration	Salt	
α-Benzoin oxime	10.0 g. per liter 95 per cent ethanol	1.0 *N*	$CuSO_4$	FB
"	"	1.0 *N*	$Cu(NH_3)_4SO_4$	FB
Cupferron	Satd. aq. soln.	1.0 *N*	$CuSO_4$	PB
"	"	1.0 *N*	$CuSO_4$ in 0.05 *N* HCl	PB
"	"	1.0 *N*	$FeCl_3$	NP
"	"	1.0 *N*	$AgNO_3$	CS
Dicyandiamidine sulfate	40 g. per liter 50 per cent ethanol	1.0 *N*	$Ni(NO_3)_2$	NP
"	"	1.0 *N*	$Ni(NH_3)_4(NO_3)_2$	DS
"	"	1.0 *N*	$CuSO_4$	NP
"	"	1.0 *N*	$Cu(NH_3)_4SO_4$	NP
Dimethylglyoxime	10 g. per liter 95 per cent ethanol	1.0 *N*	$Ni(NO_3)_2$	DS
Dinitrosoresorcinol	Satd. aq. soln.	1.0 *N*	$CoCl_2$	NP
"	"	1.0 *N*	$CuSO_4$	NP
"	"	1.0 *N*	$FeCl_3$	NP
8-Hydroxyquinoline	10 g. per liter 95 per cent ethanol	1 0 *N*	$MgSO_4$	NP
"	"	5 per cent 1.0 *N*	NH_4OH—5 ml. $MgSO_4$—95 ml. AcONa—2 g.	CS
"	"	1.0 *N*	$ZnSO_4$	GB
"	"	1.0 *N*	$Al_2(SO_4)_3$	FB
"	"	1.0 *N*	$AlCl_3$	PB
"	"	1.0 *N*	$CdSO_4$	GB (121)
"	"	10 per cent 1.0 *N*	AcOH—2 ml. $CdSO_4$—98 ml. AcONa—2 g.	GB (99, 125)
"	"	1.0 *N*	$CuSO_4$	GB (137)
"	"	10 per cent 1.0 *N*	AcOH—2 ml. $CuSO_4$—98 ml. AcONa—2 g.	PB
"	"	1.0 *N*	$CdSO_4$—100 ml. AcONa—2 g.	GB (123)
"	"	1.0 *N*	$ZnSO_4$—100 ml. AcONa—2 g.	GB (133)
Nitron	5 g. per liter 95 per cent ethanol	1.0 *N*	KNO_3	F
"	"	1.0 *N*	KNO_3 in 0.13 *N* AcOH	DS

TABLE 2—*Concluded*

PRECIPITANT IN GEL		DIFFUSING SOLUTION		STRUCTURE
Material	Concentration	Concentration	Salt	
Nitroso-β-naphthol*	4 g. per liter 60 per cent ethanol	1 0 *N*	$CoCl_2$	CS
"	"	1 0 *N*	$Ni(NO_3)_2$	PB
Phenylthiohydantoic acid	Satd. aq. soln	1 0 *N*	$CoCl_2$	FB (169)
"	"	1 0 *N*	$Ni(NO_3)_2$	DS (172)
"	"	1 0 *N*	$CuSO_4$	CS
"	"	1 0 *N*	$Pb(NO_3)_2$	CS

* This gel consisted of 1 g. of agar dissolved in 20 g. of the solution of the precipitant and 80 g. of water. All others contained the same amount of agar, but 10 g. of the solution of precipitant and 90 g. of water.

diffusing solution was nickel nitrate. Tube 18 was the same except for being neutral. Tube 30 was similar to tube 14 except that the diffusing solution and precipitant were interchanged in position. Tube 34 contained a gel made slightly basic from sodium silicate, acetic acid, and potassium nitrate. Tube 41 was the same except for being acidic. The diffusing solution in both cases was nitron in 1.0 *N* acetic acid. Tube 55 is the familiar cupric chromate in agar.

DISCUSSION OF RESULTS

It is evident from the data presented that the precipitates formed in gels with organic precipitants show several types of structure. In many cases for which photographs are not shown these were not as well defined as the ones selected but they were distinctly evident.

Under the conditions studied salts of α-benzoin oxime, 8-hydroxyquinoline, and phenylthiohydantoic acid gave the best bands. Some of these are shown in tubes 99, 125, 137, 169, 335, 353 and 364. Cupferron and nitroso-β-naphthol gave noticeable bands in a few cases but they were so close together and the gels so dark that clear photographs were unobtainable. These two compounds seemed to decompose readily giving dark gels. In some cases no precipitate was obtained with dicyandiamidine sulfate or dinitrosoresorcinol. If one was formed it generally assumed a discrete structure (4), although in a few cases there was a slight indication of bands. The nickel salt of phenylthiohydantoic acid shown in tube 172 illustrates a discrete structure. Tubes 14, 18, and 30 show that bands of nickel dimethylglyoxime form with the organic compound either in the gel or above it. All other organic precipitants failed to give this type of structure if in the solution diffusing into the gel.

Nitron nitrate was the only precipitate not giving noticeable bands in at least one type of gel. Tubes 344, 347, and 351 show the fern-like

FIG. 1. RHYTHMIC PRECIPITATION WITH NITRON NITRATE AND NICKEL DIMETHYLGLYOXIME

Tubes 41 and 34, nitron nitrate; tubes 14, 18, and 30, nickel dimethylglyoxime

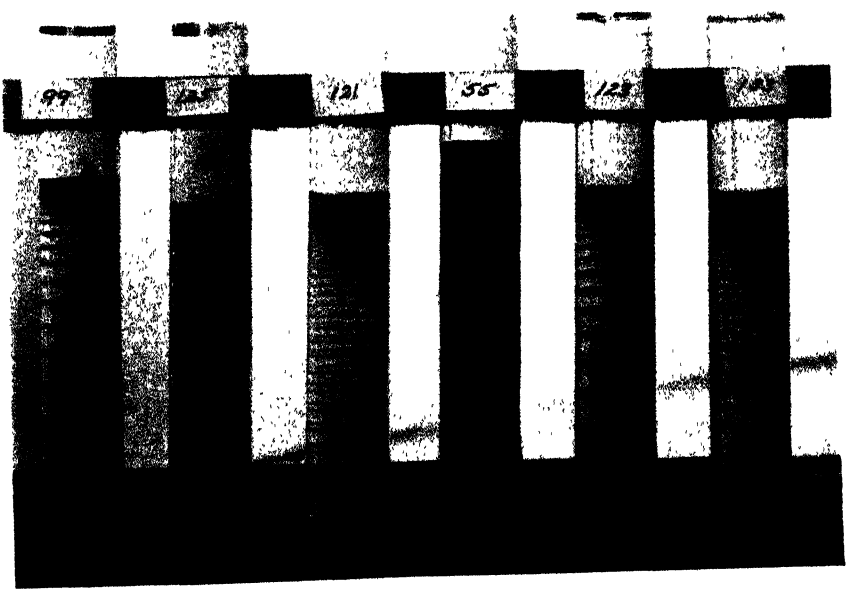

FIG. 2. RHYTHMIC PRECIPITATION WITH 8-HYDROXYQUINOLINE

Tube 99, cadmium salt of 8-hydroxyquinoline (kept in the dark); tube 125, cadmium salt of 8-hydroxyquinoline (kept in the light); tube 121, cadmium salt of 8-hydroxyquinoline; tube 55, cupric chromate; tube 123, cadmium salt of 8-hydroxyquinoline; tube 133, zinc salt of 8-hydroxyquinoline.

structures obtained. The more basic the gel the larger the crystals grew. Tubes 34 and 41 also show this precipitate, but in this case the solution of nitrate was added to the gel. Here the resulting structure is more moss-like in appearance and extends only a short distance below the surface of the gel. A well-formed, isolated crystal is shown in tube 41.

Tubes 123 and 133, containing respectively the cadmium and zinc salts of 8-hydroxyquinoline, show a helicoid variation from bands not frequently encountered. Also twin bands are shown in tube 121.

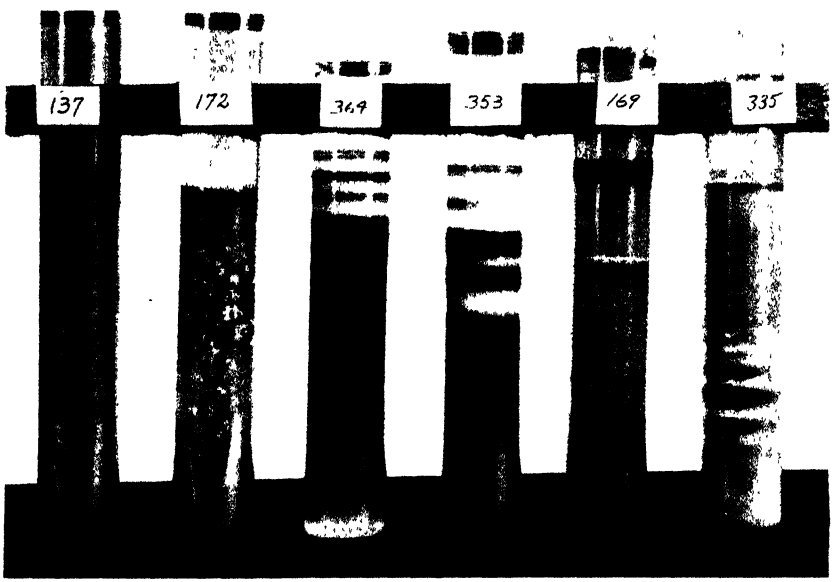

FIG. 3. RHYTHMIC PRECIPITATION WITH VARIOUS ORGANIC PRECIPITANTS

Tube 137, cupric salt of 8-hydroxyquinoline; tube 172, nickel salt of phenylthiohydantoic acid; tube 364, cupric salt of α-benzoin oxime; tube 353, cupric salt of phenylthiohydantoic acid; tube 169, cobalt salt of phenylthiohydantoic acid; tube 335, mercuric salt of phenylthiohydantoic acid.

Although the silica gels were made from both a commercial liquid water glass and from solid sodium silicate, no particular difference was evident in the structures obtained. With the exception of 8-hydroxyquinoline, the precipitants producing banded precipitates did so equally well in the different gels. This one reagent gave the best bands in agar. Keeping one set of tubes in the dark did not yield structures differing appreciably from those formed in the light. For the latter an occasional precipitate indicated some sensitivity to light resulting in some darkening.

No explanation is offered for the fact that different types of structures were obtained for different combinations, nor for the variation in quality of bands. Duplicate tubes did not always show equally good results.

Altogether several hundred tubes were prepared with considerable variation in conditions, such as acidity, concentration, and kind of gel, and the data presented were selected as being representative of all that available.

FIG. 4. PRECIPITATION WITH NITRON NITRATE

SUMMARY

As a result of a study of the formation in gels of precipitates with certain organic compounds, the following conclusions were reached:

1. Different types of structures were obtained in different cases.
2. Of the combinations forming bands not all were equally good. Nitron nitrate showed no noticeable bands.
3. The best results were obtained with the precipitant in the gel.
4. Bands were obtained in both agar and silicic acid gels. 8-Hydroxyquinoline gave better bands in agar.
5. Several good spirals and twin bands were obtained.
6. Light produced no apparent effect on the type of structure obtained.

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A QUANTITATIVE SPECTRO-PHOTOELECTRIC ANALYTICAL METHOD APPLIED TO SOLUTIONS OF CHLOROPHYLLS *a* AND *b*

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The accurate photoelectric method for comparison of low light intensities, described by Zscheile, Hogness, and Young (3), has been used to obtain quantitative analytical data for chlorophyll components *a* and *b* and their mixtures in 90 per cent acetone solution (10 per cent water). This solvent was chosen because extracts of the green and yellow plant pigments from fresh leaf material are easily obtained in aqueous acetone solution.

The absorption spectra of components *a* and *b* in ether solution (figure 1) were measured from λ 3950–7800 A. U. with an accuracy of 2.0 per cent (1.0 per cent at the absorption maxima).[2] Comparison of figure 1 with the first graphs of figures 3 and 4 shows that the absorption spectra of *a* and *b* in 90 per cent acetone solution are very similar to those in ether solution. The maxima of the principal bands are shifted 25 A. U. toward the red when the solvent is changed from ether to 90 per cent acetone. These data were useful in the choice of wave lengths for analysis of mixtures.

According to Lambert's law, the amount of radiant energy absorbed in a homogeneous medium is expressed by the equation:

$$I_x = I_0 \times 10^{-\beta x}$$

or

$$\log \frac{I_0}{I_x} = \beta x$$

In this equation,

I_0 = intensity of light transmitted by solvent-filled cell.
I_x = intensity of light transmitted by solution-filled cell.
x = thickness of absorption cell in centimeters (4.25 cm.).
β = specific light absorption coefficient.

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[2] Details of the absorption spectra measurements and of the preparation of components *a* and *b* are presented in reference 2.

When β is proportional to the concentration, c (in grams per liter), Beer's law is obeyed and

$$\beta = \alpha c$$

Then,

$$\log \frac{I_0}{I_x} = \alpha c x$$

or

$$\alpha = \frac{\log \frac{I_0}{I_x}}{cx}$$

The logarithm is to the base 10. The absorption coefficient, α, is expressed in liters per gram centimeter.

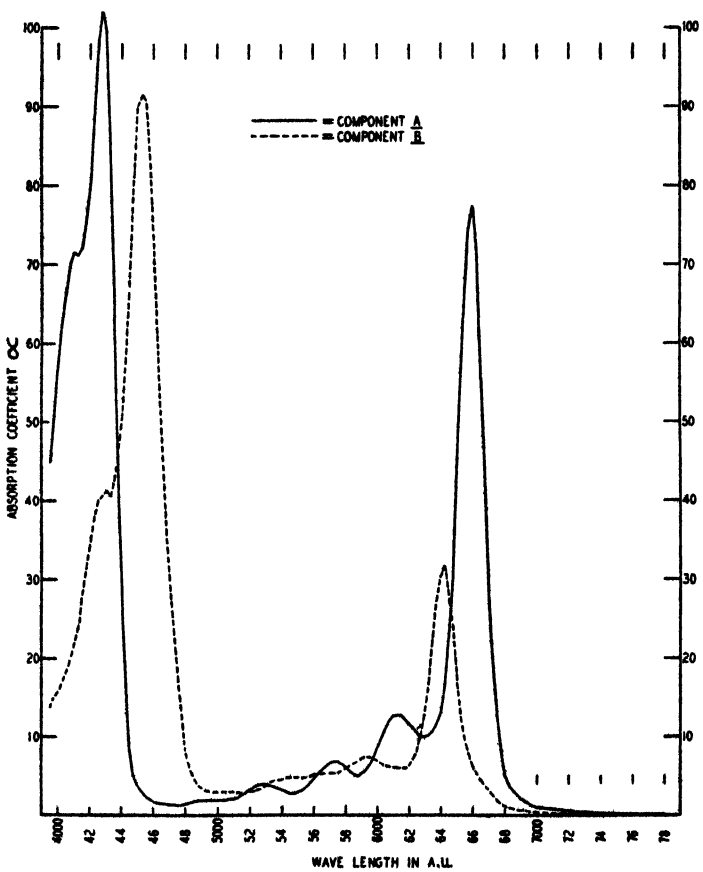

FIG. 1. ABSORPTION SPECTRA OF CHLOROPHYLLS a AND b IN ETHER

ACCURATE ANALYSIS OF MIXTURES OF CHLOROPHYLLS *a* AND *b*

For spectro-photoelectric analysis of mixtures of chlorophylls *a* and *b* for which neither the total chlorophyll ($a + b$) concentration nor the ratio of *a* to *b* is known, it is necessary to know the values of α at two carefully chosen wave lengths. The wave length 4400 A. U. was chosen for total chlorophyll ($a + b$) determination because the light absorption coefficient is the same for both components at this wave length (see figure 3, first graph). For determination of the ratio, *a* to *b*, two wave lengths, 4100 and 4270 A. U., were selected in the spectral region where there is a great difference in the absorption coefficients of *a* and *b*. Determinations at these two wave lengths serve as checks upon each other. These wave lengths were chosen in the violet rather than in the red region (where the absorption difference is also great), because narrower spectral regions may be isolated by the monochromator at the shorter wave lengths. The width of the spectral regions used in these measurements was 7 A. U. or less.

Chlorophylls *a* and *b* were isolated in the pure state and weighed samples of the best preparations of these were dissolved in ether to form solutions of known concentrations. Aliquots of these solutions were measured volumetrically and mixtures of the components *a* and *b* were made, having the following compositions: 5, 10, 25, 50, 75, 90, and 95 per cent *a*. The ether was evaporated in a stream of dry nitrogen and the chlorophyll was dissolved in 90 per cent acetone, measured volumetrically. Such dilutions were made that the values of $\frac{I_0}{I_x}$ were approximately 2.00 at the wave lengths employed. The accuracy of the concentration values was 1.0 per cent, or better.

Before each measurement of light intensity, the electrometer vane (3) was returned to the zero position by a closing of the shutter between the photocell and the second slit of the monochromator. I_0 was measured before and after I_x and the measurements were averaged for the final value of I_0. The average of two determinations of $\log \frac{I_0}{I_x}$ was used as a final value. Measurements of I_0 and $\log \frac{I_0}{I_x}$ have precisions of better than 0.5 per cent and 1.0 per cent, respectively.

When very accurate data are desired, the absorption cells should be tested at least once daily in regard to their relative light transmissibilities at the wave lengths employed. Both cells are cleaned, filled with solvent, and the intensities of light transmitted by them are measured. Those used in these experiments differ by 1.5 to 4.0 per cent. This difference varies according to the wave length and the position of the cell. Suitable

corrections are made on all values of I_0 so that the effect of this difference between the cells is cancelled.

In figure 2, the experimental values of α, determined from the mixtures of known composition and from solutions of the pure components, are plotted against composition. It is evident that the values of α for any one wave length fall on a straight line and therefore that Beer's law is

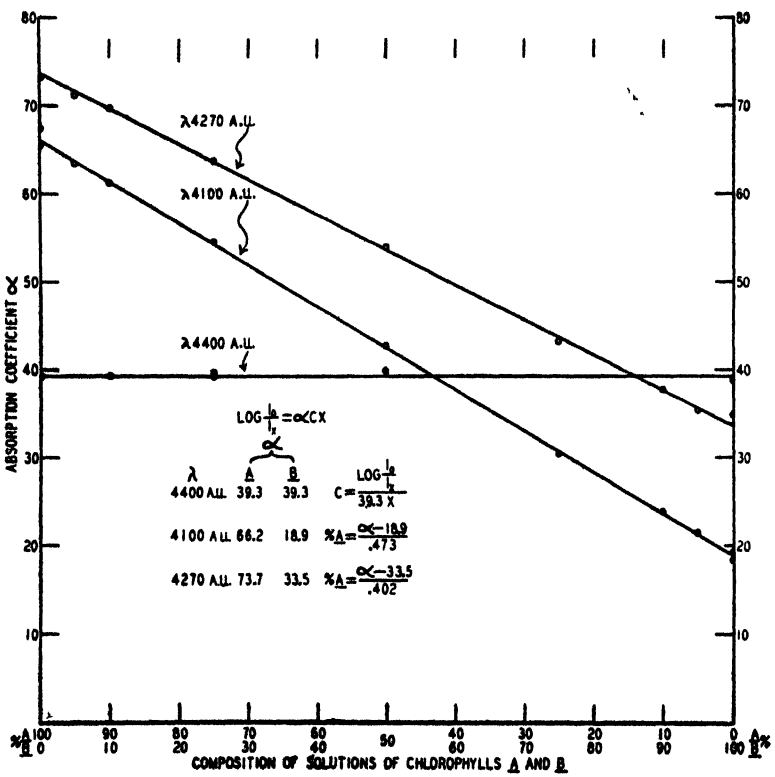

FIG. 2. QUANTITATIVE SPECTRAL ANALYSIS OF MIXTURES OF CHLOROPHYLLS *a* AND *b* IN 90 PER CENT ACETONE

valid for light of these three wave lengths at the concentrations employed (0.0010 to 0.0030 g. per liter).

The α values at λ4400 A. U. lie on a horizontal line and are independent of composition. The final values of α for pure *a* and *b* were taken from the intersections of these straight-line curves with the ordinate axes, and are thus more accurate than single observations on the pure components. In the table of figure 2 are the final values of α for *a* and *b* at the wave lengths 4400, 4100, and 4270 A. U. and equations (of the straight-line curves of figure 2) for calculation of total chlorophyll ($a + b$) concentra-

tion and percentage component compositions of unknown solutions of *a* and *b*.

Using the final values of α at λ4100 and 4270 A. U., the percentage compositions of all the mixtures were calculated from the experimental data. These are presented in table 1. The greatest deviation from the true composition is 1.2 per cent. When the analyses for both wave lengths are averaged, the deviation is only 1.0 per cent.

TABLE 1

Spectral analysis of chlorophylls a and b in 90 per cent acetone

$$\log \frac{I_0}{I_x} = \alpha c x$$

WAVE LENGTH	α		COMPOSITION IN TERMS OF *a*								
			Knowns $a + b$							Unknowns $a + b$	
										Example	
	a	*b*	5 per cent	10 per cent	25 per cent	50 per cent	75 per cent	90 per cent	95 per cent	1	2
A.U.											
4100	66.2	18.9	5 50	10.5	24.3	50.3	75.3	89.9	94.2	65.3	63.5
4270	73.7	33.5	4.73	10.4	24.1	50.7	75.6	90.3	93.8	66.7	65.0
Average per cent composition.....			5.11	10.45	24.2	50.5	75.45	90.1	94.0	66.0	64.25

ANALYSIS OF UNKNOWNS

Two unknown mixtures of *a* and *b* (neither total concentration nor composition known) were analyzed and the results are presented in table 1. Determinations at the two wave lengths agree within 1.5 per cent. Thus, it is possible to analyze mixtures of chlorophylls *a* and *b* by this spectrophotoelectric method with great accuracy and to obtain the percentage composition with an error of less than 1.0 per cent.

SUPPLEMENTARY ANALYTICAL METHOD

To estimate, with considerable accuracy, the amount of one component present as an impurity in a preparation of the other, the following supplementary method is useful.

For the same mixtures that were used in the absolute determination of α, the absorption curves were measured in the blue and red regions of the spectrum (λ4200–4800 A. U. and λ6300–6700 A. U.) where the absorption differs most for the two components. Determinations of $\frac{I_0}{I_x}$ were made with an accuracy of 1.5 per cent at intervals of 25 A. U. These curves are presented in figures 3 and 4. In the first graphs of figures 3

and 4, are the curves of the pure components, *a* and *b*. The dotted curve of pure *a* is repeated in each graph of figure 3 for comparison with the mixture curves. Similarly, the dotted curve of pure *b* is repeated in figure 4.

The region of λ4200–4800 A. U. is useful for detection of impurities of *b* in preparations of *a* (fig. 3). Five per cent of *b* may be detected easily by the appearance of the 4560 A. U. band of *b*. As the percentage of *b* increases to 50 per cent, the 4560 A. U. band becomes more prominent and the intensity of the 4300 A. U. band of *a* decreases.

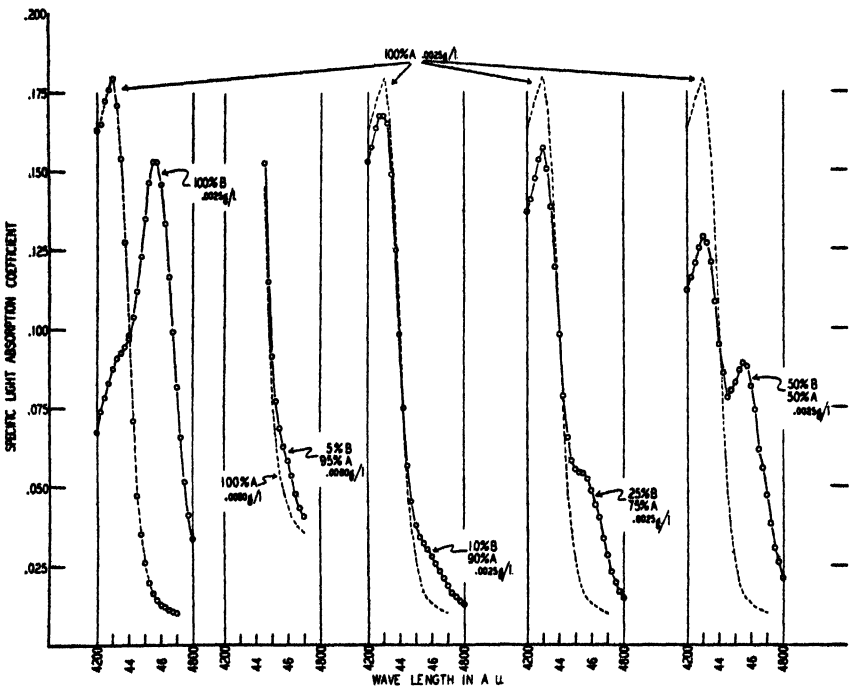

FIG. 3. LIGHT ABSORPTION OF MIXTURES OF CHLOROPHYLLS *a* AND *b* IN 90 PER CENT ACETONE

To detect impurities of component *a* in preparations of *b*, the region of λ6300–6700 A. U. may be used to best advantage (figure 4). The spectrum is appreciably changed in this region when 5 per cent *a* is present and the deviation from the spectrum of pure *b* becomes greater as the percentage of *a* increases.

The concentration of the solution need not be known accurately for detection of considerable contamination of one component by another. This fact makes the supplementary method useful in following the purity of a preparation through the various steps of the isolation procedure.

Ghosh and Sen-Gupta (1) measured the molecular extinction coefficients

of chlorophylls *a* and *b* (prepared by Stoll) and their mixtures in acetone solution with a König-Marten spectrophotometer. Since their method of light intensity comparison was visual, it would not have the precision and accuracy of the photoelectric method over a wide range of wave lengths. In such a visual method, the monochromatic quality of the

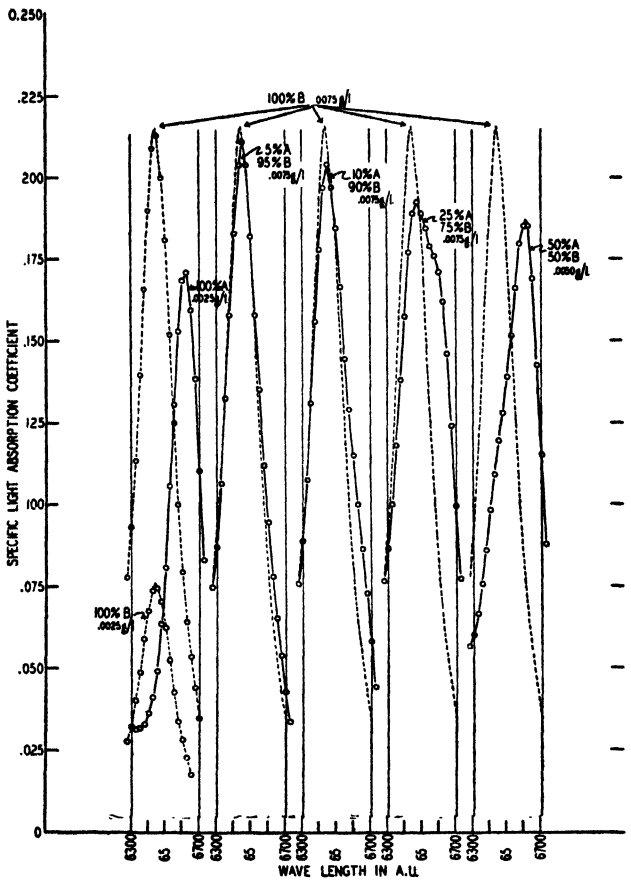

FIG. 4. LIGHT ABSORPTION OF MIXTURES OF CHLOROPHYLLS *a* AND *b* IN 90 PER CENT ACETONE

light could not be so high as in the photoelectric method used above. Their measurements were taken at such great intervals of wave length, especially in the blue region of the spectrum, that small differences in the absorption bands could not be detected. For this reason, and particularly because of the improved preparative methods of chlorophyll component separation (2), the purity of their components is questionable.

The spectro-photoelectric analytical method, as demonstrated here, undoubtedly has a wide field of usefulness, particularly in certain problems of biochemistry. By extension of the method into the ultra-violet region, as is possible with the particular monochromator and photocell used in this work, the purity of preparations of hormones, vitamins, enzymes, and other colorless compounds which are difficult to isolate in the pure state, could probably be quickly followed during preparative processes. The method will also be useful in identification of such compounds whose formulas are unknown. Mixtures of colored substances whose solutions obey Beer's law may be analyzed quickly and easily.

Similar studies on the yellow plant pigments are now in progress. It is hoped that this work, when completed, may be combined with the results reported in this paper to make possible a simpler quantitative analysis for all of the yellow and green pigments of the leaf.

SUMMARY

1. By an accurate spectro-photoelectric method, quantitative light absorption data were obtained for pure chlorophylls *a* and *b* and their mixtures. The percentage composition of unknown mixtures of components *a* and *b* were determined with an accuracy of better than 1.0 per cent.

2. From light absorption measurements at λ4400 A. U., the total chlorophyll ($a + b$) concentration is calculated. The ratio of *a* to *b* is calculated from measurements at λ4100 or 4270 A. U.

3. Experimental details are discussed which are essential for a high degree of accuracy.

4. It is shown that Beer's law is valid for chlorophyll solutions in 90 per cent acetone over a narrow range of concentrations.

5. A supplementary analytical method, accurate to 5 per cent, is useful for estimation of mixture compositions.

The writer is thankful to Dr. T. R. Hogness for suggestions given during the development of this method.

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STUDIES ON GLASS. VIII

The Coefficient of Thermal Expansion of Boron Trioxide

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For these studies on glass, which are now being carried on at Stanford University, boron trioxide was selected a few years ago as a typical inorganic, glass-forming material. The results of an extensive study of its heat capacity have been presented in an earlier paper by Thomas and Parks (4). With increasing temperatures, the specific heat at constant pressure was found to undergo an increase of more than 60 per cent between 215° and 270°C. Below this transition region the boron trioxide was a hard glass with a mean atomic heat of 3 to 4 calories, depending upon the temperature and the previous heat treatment of the material; above the transition it was an extremely viscous liquid with an atomic heat approximating the Dulong-Petit value.

In view of these interesting results a number of other physicochemical properties of boron trioxide are now being investigated in this laboratory. In the present paper we shall give some of the data which have been obtained in a study of the cubical coefficient of thermal expansion over the temperature range 100° to 320°C.

METHOD AND APPARATUS

The samples of boron trioxide used in this investigation were prepared from Merck's c. p. anhydrous B_2O_3 (impurities guaranteed to be less than 0.01 per cent). This material was always heated in a platinum crucible for one to two hours at a temperature of about 1200°C. in order to drive off the last traces of water and to eliminate gas bubbles. The molten oxide was next poured into a small cylindrical mold, made out of copper foil, and permitted to cool to room temperature in a desiccator containing phosphorus pentoxide. The copper foil was then stripped from the boron trioxide glass and the latter was smoothed down a little in a lathe. These small cylinders usually contained from 5.5 to 7.5 gm. of oxide, equivalent to 3 or 4 cc. in volume.

A simple dilatometer, with mercury as the dilatometric fluid, was em-

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ployed in the determinations of the coefficient of thermal expansion. It was made entirely out of "tool" steel and consisted essentially of a stout cylindrical can of about 2.0 cm. diameter and 6 cc. capacity. A top fitted into this can by means of a tapered, vacuum-tight joint and was held firmly in position by an adjustable nut. A steel capillary tube, welded through the top, projected upward for a distance of 15 cm. and ended in a small horizontal nozzle; it served as a means of ejecting the excess mercury as the dilatometer was heated to successively higher temperatures and the contents of the steel can underwent expansion.

The large, electrically-heated copper block which Thomas and Parks (4) developed for their specific heat measurements was employed in the present investigation as an adjustable thermostat. The can of the dilatometer was placed within the central cavity of this block with the steel capillary passing upwards through a hole so that the exit nozzle was in the outside air. A small glass weighing bottle then served to collect the mercury droplets as they were expelled at this nozzle during the heating of the copper block between successive steps in temperature.

Measurements of the temperatures were made with calibrated thermocouples in conjunction with a White double-combination potentiometer. A chromel–alumel thermocouple, having one junction fastened to the outside wall of the dilatometer can and the other imbedded in the copper block, served to tell when the dilatometer was at the same temperature as its surroundings. A platinum–platinrhodium thermocouple with one junction on the outside of the dilatometer and the other at 0°C. was used for measuring the actual temperatures to 0.01°C.

The procedure in filling the dilatometer for the expansion measurements was extremely simple. A prepared cylinder of the boron trioxide glass was first placed in position in the dilatometer can, the top was fitted on, and the whole instrument was evacuated to 0.01 mm. by a "Cencomegavac" oil pump. Clean, freshly heated mercury was then caused to flow into the free space of the dilatometer by raising the level of a mercury reservoir which was connected to the side tube of the evacuating and filling system. The dilatometer and contents were next heated under reduced pressure to over 300°C. in order to remove any possible air bubbles within the instrument, and afterwards a small amount of mercury was introduced as the dilatometer was quickly cooled down to room temperature by quenching in a water or alcohol bath.

After such preparations the dilatometer was placed within the copper block and the latter was heated electrically from 100°C. up to about 300° or 325°C. in seven to ten steps. These steps often covered temperature intervals as large as 32°C., where the boron trioxide was either a hard glass or a very viscous liquid and the expansion coefficient was not changing greatly. On the other hand, the temperature steps within the range

210° to 270°C. were usually kept between 15° and 20°C., as here the coefficient was increasing rapidly. Since boron trioxide is a very poor conductor of heat, it was important to allow sufficient time to elapse at each step for complete equalization of temperature within the sample. Accordingly, in some cases the temperature in the copper block was maintained constant for periods as long as two and a half hours.

The calculation of the coefficient of expansion of the boron trioxide from the weights of the mercury ejected between successive temperatures was simple. At an initial temperature, T_1, the volume of the mercury in the dilatometer plus the volume of the oxide sample was equal to the volume of the dilatometer itself; or in equation form we have

$$\left(\frac{1}{d_1}\right) W_1 + V_{1\,(\text{oxide})} = V_{1\,(\text{dilatometer})} \tag{1}$$

where d_1 and W_1 represent, respectively, the density and weight of the mercury in the dilatometer. At a higher temperature, T_2, we may similarly write

$$\left(\frac{1}{d_2}\right) W_2 + V_{2\,(\text{oxide})} = V_{2\,(\text{dilatometer})} \tag{2}$$

The weight of mercury which is ejected from the dilatometer in heating from T_1 to T_2 is, of course, $W_e = W_1 - W_2$. By making use of this fact and subtracting the first equation from the second, we then obtain

$$\Delta V_{\text{oxide}} = \Delta V_{\text{dilatometer}} - \left(\frac{1}{d_2} - \frac{1}{d_1}\right) W_1 + \frac{W_e}{d_2} \tag{3}$$

The volume increase of the dilatometer over the temperature ranges of this study was first determined in two independent series of measurements, which were carried out in the absence of a boron trioxide sample. The necessary data for the density of mercury at the various temperatures were taken from the Landolt-Börnstein "Tabellen" (2).

From the values of ΔV_{oxide} (obtained by equation 3) the cubical coefficient of expansion, α, may be evaluated. By definition

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

However, for the rather small temperature steps employed in the present investigation $\frac{\Delta V_{\text{oxide}}}{\Delta T}$ approaches $\left(\frac{\partial V}{\partial T}\right)_p$; and accordingly we have employed here the approximation

$$\alpha = \frac{2}{V_2 + V_1}\left(\frac{\Delta V_{oxide}}{T_2 - T_1}\right) \tag{4}$$

which will not involve us in any great error.

EXPANSION DATA

Expansion determinations were made upon several different boron trioxide samples in the course of our investigation, but naturally a number of these measurements were rather preliminary in character. In the present connection we shall restrict ourselves for the purposes of brevity to a consideration of the data for the last two samples studied.

TABLE 1

The cubical coefficient of expansion of boron trioxide

UNANNEALED		PARTIALLY ANNEALED		CAREFULLY ANNEALED	
Sample 1, under various conditions					
degrees C.	α	*degrees C.*	α	*degrees C.*	α
113.1	0.41 (10^{-4})	122.1	0.48 (10^{-4})	123.7	0.52 (10^{-4})
139.7	0.37 (10^{-4})	156.9	0.55 (10^{-4})	157.4	0.60 (10^{-4})
166.7	0.17 (10^{-4})	188.1	0.55 (10^{-4})	184.4	0.83 (10^{-4})
193.7	−0.17 (10^{-4})	213.3	0.83 (10^{-4})	204.4	1.08 (10^{-4})
217.8	−0.73	234.8	3.98	222.8	3.45
234.9	2.19	256.6	5.70	247.5	5.61
251.1	5.84	286.5	6.25	275.7	6.05
269.1	6.00				
290.3	6.16				
310.0	5.84				
Sample 2, under various conditions					
122.1	0.40 (10^{-4})	120.6	0.56 (10^{-4})	114.2	0.54 (10^{-4})
152.3	0.19 (10^{-4})	152.9	0.59 (10^{-4})	143.4	0.49 (10^{-4})
180.4	−0.19 (10^{-4})	177.8	0.71 (10^{-4})	171.8	0.59 (10^{-4})
204.9	−1.07 (10^{-4})	198.3	0.85 (10^{-4})	199.6	1.18 (10^{-4})
229.4	0.55 (10^{-4})	217.1	1.62 (10^{-4})	226.9	4.35 (10^{-4})
250.2	4.10	233.1	4.64 (10^{-4})	250.0	6.13
270.0	6.22	249.1	6.64 (10^{-4})	270.0	5.92
293.8	6.35				

Sample 1 contained 6.3 g. of the oxide. After its installation in the dilatometer it was first heated to about 325°C. and then quickly cooled by quenching the dilatometer in water. The results of a series of expansion measurements made upon the material in this condition are given in the first part of table 1 under the heading "unannealed." The sample was next cooled from 300°C. down to room temperature at the rate of about 5°C. per hour. The subsequent series of expansion measurements

appears in the first section of table 1 under the heading "carefully annealed." Finally, the sample was cooled from 300°C. to room temperature at the rate of 25°C. per hour, after which the data for the "partially annealed" material were obtained.

Sample 2 was very similar to the preceding one, although it had been prepared from a different batch of boron trioxide. In this case the expansion coefficients for the unannealed condition were obtained after the dilatometer and contents had been heated to 325°C. and quenched in a large beaker of ethyl alcohol. The heat treatments of the sample prior

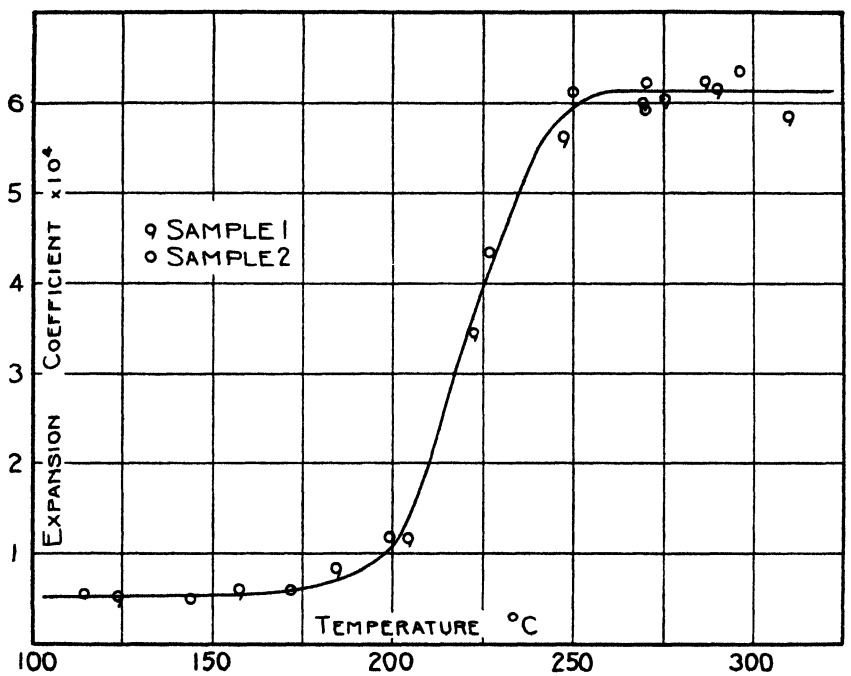

FIG. 1. SHOWING THE EXPANSION DATA FOR THE TWO SAMPLES IN THE CAREFULLY ANNEALED CONDITION

to the "carefully annealed" and "partially annealed" determinations were practically the same as in the case of sample 1. All these data appear in table 1.

In our judgment the experimental error incidental to our method of measuring the coefficient of expansion should be under 5 per cent in all cases. Any deviations between different series of data which appreciably surpass this figure should be attributed to differences in the heat treatment of the samples either prior to or during the measurements. A comparison of our various results therefore serves to bring out the great variability of the boron trioxide in the region below 260°C., where, as it

cools, the oxide begins to change over from an extremely viscous liquid[2] to a hard, glassy condition.

The glasses, after they have been "carefully annealed," undoubtedly represent fairly close approaches to internal equilibrium and accordingly the expansion coefficients obtained in this connection for the two samples are in good agreement. Likewise, the influence of strains and previous thermal history is relatively unimportant in the viscous liquid above

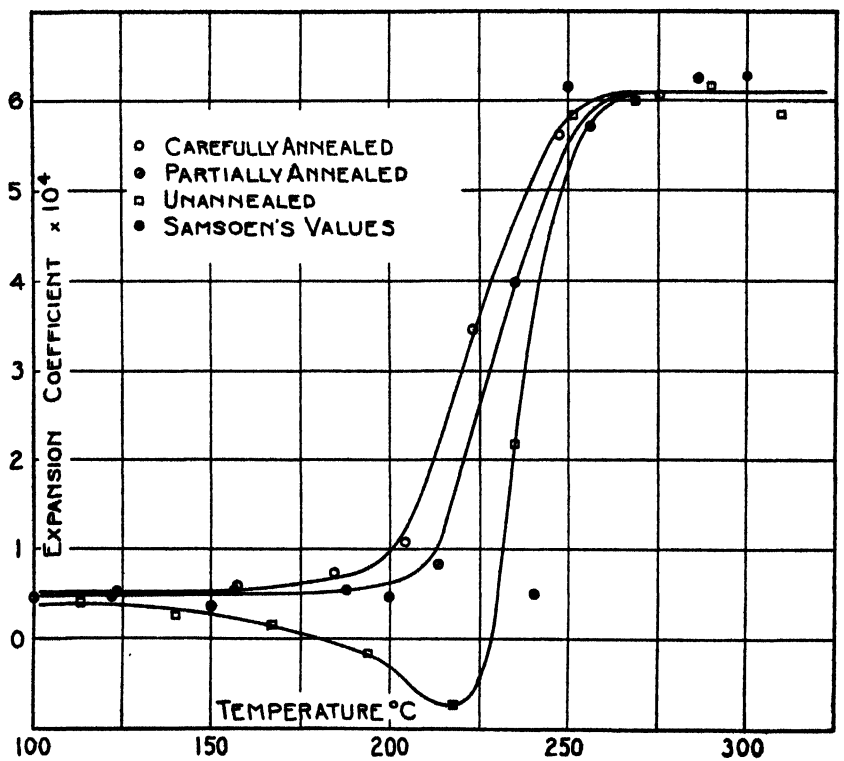

FIG. 2. SHOWING THE EXPANSION DATA OBTAINED FOR SAMPLE 1 FOLLOWING VARIOUS DEGREES OF ANNEALING

270°C., and so in this region the results of all determinations, regardless of previous treatment, are practically within the limits of experimental error. These findings are represented graphically in figure 1.

On the other hand, the glasses in the "unannealed" and "partially annealed" conditions yielded results of poorer reproducibility below 260°C. In particular, the coefficients of expansion for the unannealed glasses run decidedly below those for the carefully annealed and even assume various

[2] We have been able to make viscosity measurements upon boron trioxide down to 267°C., at which temperature $\eta = 2\ (10^{11})$ poises.

negative values between 180° and 230°C. In other words, there is actually a decrease in the volume of the glass sample within this range. Such behavior, of course, makes the subsequent rise as the viscous-liquid condition is approached even more rapid than in the case of a carefully annealed glass. The data for the "partially annealed" glasses, as might have been expected, generally lie between those for the "unannealed" and "carefully annealed" conditions. Curves for the three sets of data thus obtained in the case of sample 1 are shown in figure 2.

Some measurements of the coefficient of thermal expansion of boron trioxide within this temperature range have also been made by Samsoen (3). The values reported by him have been included for comparative purposes in figure 2 where they are represented by the solid dots. His results below 200°C. and above 260°C. are in good agreement with some of our determinations. However, between these two temperatures he obtains a much sharper transition in the expansion coefficient than we have ever found in any of our samples.

DISCUSSION

The results of this study show that for boron trioxide the cubical coefficient of thermal expansion in the viscous-liquid state is more than ten times that for the glass and that between these two states there is a transition[3] extending over a temperature range of about 50°C. Thus these expansion phenomena parallel those found by Thomas and Parks (4) in their study of the specific heats of this substance. They are also in thorough agreement with the results of some expansion measurements of an optical glass reported by Berger (1). In view of such findings it seems to us quite clear that a glass must be considered in a separate category from the undercooled viscous liquid from which it is formed.

The very marked influence of the rate of cooling from the liquid to the glassy states is also a noteworthy feature. Probably no actual glass can be considered as being in a condition of true thermodynamic equilibrium at a temperature much below its softening region; the attainment of such an equilibrium might require the lapse of almost infinite time. However, our boron trioxide glasses which were formed by careful annealing were probably not greatly removed from a condition of internal equilibrium or, in other words, they represent a good approach to stable glasses. On the other hand, the glasses which were produced by quenching the dilatometer in water or alcohol represent substances which are in a state of great strain or, we might say, which are greatly removed from the condition of internal equilibrium at lower temperatures. It is interesting to

[3] It must be realized that the coefficients of expansion reported here are mean values over temperature intervals. Such values tend to smooth out the curve and to decrease the sharpness of the change.

note that the volumes of such glasses are appreciably larger than those for the annealed, as the comparative data (table 2) for the volumes of the two samples under various conditions show.

The volumes of the unannealed glasses at room temperature are almost as great as those of the carefully annealed at a temperature within the transition region. Thus in the unannealed glass there must be a tendency for the material to undergo internal changes in the direction of a smaller volume. Nevertheless, the effects of such a tendency cannot become very noticeable at temperatures far below the softening region of the glass because the velocity of the shift toward the equilibrium point is bound

TABLE 2

The volume of the glass samples at room temperature

CONDITION	SAMPLE 1	SAMPLE 2
	cc.	*cc.*
Unannealed	3.419	3.425
Partially annealed	3.384	3.379
Carefully annealed	3.373	3.366

to be extremely low where molecular translation is infrequent. However, as the temperature of the unannealed glass approaches the softening region and the frequency of translational motion of the molecules in the structure increases markedly, this tendency of the internal equilibrium to shift towards a smaller volume predominates for a time over the general expansion tendency of the material and produces the negative values of the coefficient of expansion between 180° and 230°C.

SUMMARY

By use of a small dilatometer with mercury as the dilatometric fluid the coefficients of thermal expansion of two samples of boron trioxide have been measured between 100° and 325°C. with a probable experimental error of less than 5 per cent. The coefficient for the viscous liquid was found to be more than ten times that for the glassy state. The character of the expansion coefficient–temperature curves below 260°C. depended greatly upon the extent of the annealing during the initial formation of the glass.

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THE THERMODYNAMICS OF THE ELECTROCAPILLARY CURVE. I

The General Equations

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I. Introduction

If a difference of electric potential $\mathfrak{E}$, varying from 0 to about 1.5 volts is applied to the electrodes of a system such as

Hg	aqueous KNO_3 solution of any concentration	any constant nonpolarizable reference electrode

making the Hg|KNO_3 solution end the cathode, the surface tension σ at the Hg|KNO_3 solution boundary varies in a regular way. The measurement of σ for various values of $\mathfrak{E}$ is best carried out in the Lippmann electrometer (1). The curve obtained by plotting σ as ordinate and $\mathfrak{E}$ as abscissa is called the electrocapillary curve of the system. In practice the system may be varied by replacing the mercury by an amalgam or by some other liquid metal such as gallium, and the potassium nitrate solution by aqueous or organic solutions of any electrolytes whose cations are sufficiently electropositive not to be deposited upon the metallic phase to any appreciable extent within the range used; the electrolyte must therefore in particular be as free as possible of the ions of those metals constituting the metallic phase.

Since its discovery (2), two thermodynamic theories of the electrocapillary curve have been advanced. The first, due chiefly to Lippmann, Helmholtz and Planck (3), is that of the so-called "perfectly polarizable electrode." The second, usually referred to as the "Gibbs theory," and due chiefly to Gibbs, Thomson, Warburg, Gouy and Frumkin (4), consists in the direct application of Gibbs' adsorption theorem to the polarized electrode.

The two theories start from independent, apparently unrelated assumptions, but both lead to the same result, verified by experiment (5), that the slope of the electrocapillary curve is equal to the surface density of electric charge on the surface of the mercury in contact with the solution. Together the two theories give a good account of most of the facts of elec-

trocapillarity (6). Nevertheless they are unsatisfactory in at least two respects:

1. The theory of the "perfectly polarizable electrode" does not give an account of the variation of the electrocapillary curve with the composition of the two phases involved.

2. The "Gibbs theory," although it does take account of the composition, rests on the assumption, among others, that the mercury surface is always in equilibrium with Hg_2^{++} and Hg^{++} ions in the solution adjacent to it in the capillary. This assumption is open to question because, except for the lowest part of the ascending branch of the curve,[1] the solution in the capillary never contains an appreciable concentration of mercury salt; the values of $C_{Hg_2}{}^{++}$ calculated from the potentials applied along by far the greater part of the curve lie between 10^{-8} and 10^{-60}. This means that any Hg_2^{++} or Hg^{++} ions at all, which happen to diffuse into the neighborhood of the mercury surface in the capillary, are immediately and violently removed from the solution by electrolysis, so that actually there is anything but equilibrium with respect to these ions.[2] That in spite of this assumption the "Gibbs theory" leads to a correct result, suggests that the error is partly or wholly counterbalanced by the other assumptions, difficult to verify individually, on which that theory rests.

In short, the first theory seems to be incomplete, and the second one at least partly wrong—a situation which explains the disconcerting existence of two apparently unrelated theories leading to one correct result.

The following is an attempt to give a complete theory starting from only one special assumption, which is sufficiently realized in the Lippmann electrometer.

II. The Theory

A. The Assumptions

1. The perfectly polarizable system

Let A, figure 1, represent a system of two electrically conducting liquid phases, α and β, separated by a plane inhomogeneous boundary layer B, of finite thickness (lightly shaded portion of figure). The external surface of A is to be looked upon as bounded by a container of some nonconducting and chemically inert material. It is furthermore assumed that the interior of the system is electrically neutral as a whole. This means that any closed surface, D, in the interior, extending into the homogeneous regions

[1] For this part of the curve to be sure, where $C_{Hg_2}{}^{++}$ may reach values as high as 10^{-3}, the equilibrium $Hg \mid Hg_2^{++}$ does obtain, as shown by A. Frumkin and A. Obrutschewa (Z. physik. Chem. **136A**, 248 (1928) and K. Bennewitz and K. Küchler (Z. physik. Chem. **153A**, 443 (1931)).

[2] The author is indebted to Professor E. Lange for calling his attention to this difficulty.

of both α and β and cutting the boundary layer B perpendicularly everywhere, can contain no appreciable excess electric charge—a condition which is fulfilled by all conducting two-phase systems in equilibrium at ordinary temperatures.

Finally, the system is assumed to have the following special property: *Somewhere within the inhomogeneous boundary layer B and parallel to it, there exists a thin layer C′* (heavily shaded portion of figure 1), *which is*

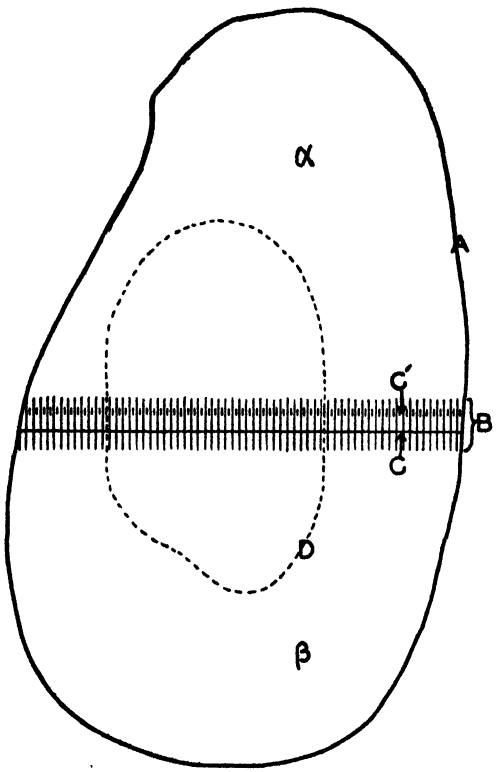

FIG. 1. SCHEMATIC REPRESENTATION OF PERFECTLY POLARIZABLE SYSTEM
B = boundary layer between phases α and β; C′ = barrier impermeable to charged particles; C = fictitious Gibbs surface; D = fictitious closed surface in interior.

impermeable in both directions to charged particles (ions, electrons) of any sort. The word "thin" in this statement means that the barrier to charged particles may be thin compared with the entire inhomogeneous layer B. The barrier C′ is evidently the layer in which the general properties of the medium change relatively abruptly from those of a metal to those of an aqueous or other solution: on one side of C′ the system, although still inhomogeneous, has entirely metallic properties; on the other side, although also inhomogeneous, it has entirely nonmetallic properties.

A necessary condition for the above special property is the following: of all the species of electrically charged particles (formed by dissociation of any of the components) present in one of the phases, say α, none may be present to any appreciable extent in the other phase β, and vice versa. This condition implies the complete absence of electrochemical equilibrium. The condition is, however, not sufficient, because its fulfillment does not preclude all electrolysis (e.g., the formation of gaseous hydrogen on a copper cathode in a solution containing H^+ but no Cu^+ or Cu^{++}, due to passage of electrons from the metal into the solution). Since electrolysis can always be brought about by applying a sufficient E.M.F. in the proper direction, a given system can possess the property mentioned only within a certain range of $\mathfrak{E}$.

A discussion of the definition and properties of the "perfectly polarizable electrode" of Planck (3) would be inexpedient here. Suffice it to say that the assumption of the above property leads to all the consequences necessary for an exact treatment of the "perfectly polarizable electrode." The property in question will therefore be designated as that of *perfect polarizability*, and any system possessing it as a *perfectly polarizable system*. The physical significance of this name lies in the impossibility of electrolysis and the attendant absence of electrochemical equilibrium. The perfectly polarizable system evidently constitutes a case intermediate between that of two conducting phases in electrochemical equilibrium as regards one or more charged species, and that of a conducting phase in contact with a dielectric.

2. Relation of the perfectly polarizable system to the electrocapillary curve

If to the electrodes of the system Hg | aqueous KNO_3 solution | 1 N KCl | Hg_2Cl_2 | Hg potentials $\mathfrak{E}$ are applied making the Hg | KNO_3 side the cathode, practically no electrolysis will take place as long as $0 \leq \mathfrak{E} \leq 1.3$ volts, because (1) the potassium nitrate solution contains no Hg_2^{++} or Hg^{++}, (2) K^+ is too electropositive to be deposited in appreciable amount (7), and (3) even after the deposition potential of hydrogen gas at atmospheric pressure ($\mathfrak{E}$ = about 0.7 volts in the example quoted) is exceeded, overvoltage keeps the hydrogen from being formed to any appreciable extent. Similar considerations apply to the other systems giving rise to electrocapillary curves in the Lippmann electrometer. The perfectly polarizable system thus constitutes an idealization which is closely approached by the real systems in question. Consequently a thermodynamic theory of perfectly polarizable systems will at the same time be a general theory of the electrocapillary curve. Any discrepancy between such a theory and the facts will be due to a deviation of the system from perfect polarizability.

But of such deviation there exists a very direct measure; it is the density of the "depolarization current" which flows upon applying the potential $\mathfrak{E}$.

If there were no depolarization current, the system would be perfectly polarizable. In a Lippmann electrometer containing alkali salt solution, the current density (at the small electrode) is very small, of the order of 10^{-4} to 10^{-3} ampere $\times$ cm^{-2}.

B. THE COMPOSITION OF THE SYSTEM

1. *Three definitions concerning composition*

(1a) *Charged components.* In a system containing electrically charged species it is possible to regard the latter as components in the thermodynamic sense. For such "charged components," as for the electrically neutral components of a system, the chemical formulas assumed are to some extent arbitrary, the *number* of components alone being fixed. Let any system in equilibrium be bounded by a non-conducting chemically inert container of variable volume. Then the number of charged components is the number of electrically charged species, the *total* amount of which within the container may be varied *independently.* Thus, the system: aqueous H_2SO_4 solution | vapor has three charged components, which may be taken as H^+, OH^-, $SO_4^=$, or H_3O^+, OH^-, $SO_4^=$, or H^+, OH^-, HSO_4^-, etc. In a binary alloy there are three charged components: the ions of the two metals and electrons.

(1b) *Electrolyte components.* No matter in what proportions the charged components are present in any system as a whole, including its inhomogeneous boundary regions, all phase interiors will remain electrically neutral, because excess charges always collect in boundary layers. The interiors of the conducting phases of a system may therefore be regarded as containing a certain number of neutral components capable of dissociation, of which the charged components are dissociation products. These neutral but dissociating components will henceforth be referred to simply as "electrolyte components," whether they are electrolytes in the ordinary sense or not. Thus the system Tl amalgam | aqueous KCl solution, which contains two electrolytes in the ordinary sense, potassium chloride and water, contains four electrolyte components, which may be taken as thallium, mercury, potassium chloride, and water.

The chemical formulas assigned to the electrolyte components are to some extent arbitrary, only the number of these components in a given system being fixed. Thus, for a system consisting of a single phase and its boundary layers, and containing p^α charged components, the number of electrolyte components is in general $p^\alpha - 1$.[3]

[3] Owing to electroneutrality the amounts of only $p^\alpha - 1$ of the p^α species can be varied independently in the phase interiors. This means that the presence of p^α charged components *in the system* demands the presence of $p^\alpha - 1$ (corresponding) components for the phase interior. But whether these $p^\alpha - 1$ components of the interior are taken to be electrically charged species, or neutral species giving rise to

(2) *Neutral components.* Any uncharged components which do not dissociate appreciably into charged species will be referred to simply as "neutral components."

The point of these definitions lies in the fact that whereas at constant temperature and pressure the state of a *system as a whole* depends upon the amounts of the neutral components and of the charged components, the state of *all the phase interiors*[4] may be regarded as depending only upon the amounts of neutral components and of the electrolyte components, that is, the electrolyte components are convenient alternatives to the charged components in the description of phase interiors apart from boundary layers.

2. *Description of the composition of the perfectly polarizable system*

Since both phases α and β of the system, figure 1, are electrically conducting, they will both contain charged components. Let p^α be the number of charged components in α, p^β the number in β, and p the total number of charged components of the system. Then, since α and β may have no charged components in common,

$$p = p^\alpha + p^\beta \tag{1}$$

Let q^α be the number of electrolyte components in α, q^β the number in β, and q the total number of electrolyte components of both phase interiors. Then, since the perfectly polarizable system behaves, as regards its charged components, like two entirely separated single phases,

$$q^\alpha = p^\alpha - 1 \tag{2.1}$$

$$q^\beta = p^\beta - 1 \tag{2.2}$$

$$q = q^\alpha + q^\beta = p - 2 \tag{3}$$

Let r^α be the number of neutral components in α, r^β the number in β, and r the total number of neutral components of the system. Then, since there is theoretically no restriction on the number or nature of the neutral components, so that the two phases may have a certain number, $r^\alpha + r^\beta - r$, in common,

$$r \leq r^\alpha + r^\beta \tag{4}$$

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the charged species by dissociation, or some of each, is immaterial, because only the number of the components is significant. Thus, if a one-phase system contains the charged components K^+, Na^+, Cl^-, NO_3^-, the amounts of only three of these ions can be varied independently in the phase interior, and so there are only three electrolyte components, KCl, KNO_3, $NaNO_3$, or KCl, NaCl, $NaNO_3$, etc.

[4] By the state of a phase interior is meant the totality of the factors affecting any events that might be caused to take place in the phase interior.

In practice one of the two phases is always metallic, so that the r neutral components will practically always be restricted to one phase, the non-metallic one, i.e., if α denotes the metallic phase, then:

$$r = r^{\beta} \tag{5}$$

The treatment will, however, proceed on the more general assumption (equation 4).

The total number, J, of components of the *system* is given by

$$J = p^{\alpha} + p^{\beta} + r = p + r \tag{6.1}$$

$$= q^{\alpha} + q^{\beta} + r + 2 = q + r + 2 \tag{6.2}$$

and the number, K, of components of the *two phase interiors* is given by

$$K = p^{\alpha} + p^{\beta} + r - 2 = p + r - 2 \tag{7.1}$$

$$= q^{\alpha} + q^{\beta} + r = q + r \tag{7.2}$$

so that, for the perfectly polarizable system,

$$K = J - 2 \tag{8}$$

In what follows, the subscript i will refer to the charged components, j will refer to the electrolyte components, and k will refer to the neutral components. In accordance with this notation, the (charged) species representing the charged components of the system will be designated by X_i^{α}, X_i^{β} or, without allocation to phase, by X_i; the electrolyte components by X_j^{α}, X_j^{β}, or by X_j; and the neutral components by X_k^{α}, X_k^{β}, or by X_k.

C. GENERAL EQUATIONS OF THE PERFECTLY POLARIZABLE SYSTEM

1. The extensive properties of the boundary layer

The values of the extensive properties such as energy, entropy, or the amount of a component, may be defined according to Gibbs for any boundary layer as follows. Imagine a geometrical surface C, lying parallel to the boundary layer B (figure 1) at an arbitrary level. This level, being arbitrary, may be regarded as defined by a variable x, denoting the distance from C to any parallel fixed level, say that of a certain mark on the containing wall of the system A. If G is the value of an extensive property such as energy, entropy, etc., for the entire space (matter filled) enclosed by the surface D (figure 1), then the corresponding value G^{ω} for the boundary layer is defined by:

$$G = G^{\alpha} + G^{\beta} + G^{\omega} \tag{9}$$

where G^{α} denotes the energy, entropy, etc., which the space bounded by C and that part of D which lies in α *would have if* the matter contained in it

remained homogeneous up to C, and G^β denotes the same for β. Any G^ω thus defined evidently depends upon the position of the fictitious surface C, and is therefore a function of x. In a perfectly polarizable system the only G^ω values of much physical interest are those for which the surface C is placed within the physical barrier C′ separating the metallic from the nonmetallic media. The exact definition of this level, which will be designated as the physical dividing surface of the system, and which, for a given state of the boundary layer, is characterized by a constant value of x, $x = x'$, is given on p. 124. From p. 124 on, all G^ω values will definitely and finally be referred to the physical dividing surface $x = x'$, but until then x will be regarded as arbitrary.

It may be noted that according to the above definition

$$V = V^\alpha + V^\beta \tag{9.1}$$

where V denotes the volume of the space within D (figure 1). As a result the volume of the boundary layer, V^ω, is always zero, and thus occupies a special position among the extensive properties G^ω.

2. *The charge of the double layer*

The space bounded by the fictitious surface C and that part of D which lies in α in general contains a certain net electric charge carried by charged particles accumulated near C; denote this charge by θ^α. If Ω is the area cut out of C by the closed surface D, the surface density of the charge in question is θ^α/Ω; set $\theta^\alpha/\Omega = \epsilon^\alpha$. Quantities θ^β and $\epsilon^\beta = \theta^\beta/\Omega$ may be similarly defined. θ^α, θ^β and ϵ^α, ϵ^β are regarded as the charges and charge densities, respectively, of the two sides of the double layer, *referred to the arbitrary surface* C; since these quantities are so referred, they are, like the G^ω, functions of x, of greatest physical interest for $x = x'$.

3. *The electroneutrality of the double layer*

From the initial assumption (p. 112) that the space bounded by the closed surface D is electrically neutral as a whole, it follows that if this space is divided into two parts by any surface whatever, as, for instance, C, the excess charges in the two parts are equal and opposite. Hence

$$\theta^\alpha + \theta^\beta = 0 \tag{10.1}$$

$$\epsilon^\alpha + \epsilon^\beta = 0 \tag{10.2}$$

i.e., the double layer as a whole is electrically neutral.

This condition of electroneutrality can be obtained in a different form as follows. Let n_i denote the number of *equivalents* of any charged component, X_i, contained within D. Then, by equation 9:

$$n_i = n_i^\alpha + n_i^\beta + n_i^\omega \tag{11}$$

Furthermore let the quantity w_i be defined by

$$w_i = \frac{z_i}{|z_i|} \tag{12}$$

where z_i denotes the valence of X_i with sign included (e.g., $z_{Ca}^{++} = 2$, $z_{SO_4}^{=} = -2$); w_i is evidently equal to $+1$ for each positively charged component and to -1 for each negatively charged component. If equation 11 is multiplied by w_i and the sum taken over all p charged components, the result is

$$\sum_{i=1}^{p} w_i n_i = \sum_{i=1}^{p} w_i n_i^{\alpha} + \sum_{i=1}^{p} w_i n_i^{\beta} + \sum_{i=1}^{p} w_i n_i^{\omega} \tag{13}$$

The term on the left vanishes because the space within D is electrically neutral as a whole, and so do the first two terms on the right because the phase interiors are electrically neutral; this leaves

$$\sum_{i=1}^{p} w_i n_i^{\omega} = 0 \tag{14.1}$$

expressing the electroneutrality of the double layer. The introduction of the surface densities of the X_i (in equivalents per unit area) defined by $\Gamma_i = n_i^{\omega}/\Omega$ into equation 14.1, gives the alternative form

$$\sum_{i=1}^{p} w_i \Gamma_i = 0 \tag{14.2}$$

4. In a perfectly polarizable system the charge of the double layer can be varied independently of the state of the interiors of the two phases

If this proposition is true for θ^{α}, θ^{β} referred to the physical dividing surface $x = x'$, it is obviously true for any other value of x. Its truth for $x = x'$ is evident from the following. Suppose there were in contact with the phase α a series of electrodes, one for each of the X_i^{α}, permitting its addition to or removal from the system. Suppose the same for β. Now through an electrode in contact with α cause Δn_i^{α} equivalents of X_i^{α} with an electric charge of $w_i^{\alpha} F \Delta n_i^{\alpha}$ (F = Faraday's equivalent) coulombs to enter the system, simultaneously introducing an equal number of equivalents Δn_i^{β} of some oppositely charged component X_i^{β} into β. Since no electrolysis can take place, the result will be that an electric charge of $w_i^{\alpha} F \Delta n_i^{\alpha}$ will distribute itself (1) along the α side of C, (2) along the free surface of α, and that an equal and opposite charge, $w_i F \Delta n_i^{\beta}$, will dis-

tribute itself similarly in β.[5] Moreover, although only one of the X_i^α be originally introduced into each phase, all of them will in general take part in this distribution (cf. equations 14.1 and 14.2). Consequently the concentrations of the X_j^α, X_j^β in the phase interiors will in general be changed by the introduction of the charges $w_i^\alpha F \Delta n_i^\alpha$, $w_i^\beta F \Delta n_i^\beta$. Finally, owing to shifting of the absorption equilibria of the X_k by the change in charge density at the double layer and at the free surfaces, the concentrations of the X_k in the phase interiors will also be changed. But the concentrations of the X_j and X_k in the phase interiors may be restored to their original values, leaving the charge of the double layer at a new value, $\theta^\alpha + \Delta\theta^\alpha$, $\theta^\beta + \Delta\theta^\beta$.

Such a process can be carried out only in the absence of electrochemical equilibrium, because otherwise electrolysis will always take place. In systems *with* electrochemical equilibrium, the state of the boundary layer including θ^α, θ^β is always *completely* determined by the state of the adjacent phase interiors.

The process described is essentially the one taking place in a Lippmann electrometer when a potential is applied, except that in the electrometer it is not necessary artificially to restore the concentrations in the phase interiors to their original values, the concentration changes produced being insignificant as long as deviations from perfect polarizability remain small.

5. Deduction of the fundamental equations for the boundary layer and for the surface tension

A "fundamental equation" of the Gibbsian type for the energy of the boundary layer E^ω (defined according to equation 9), will express E^ω as a function of the entropy of the boundary layer S^ω, the extent of the surface Ω, and the amounts of the various components adsorbed. In order to obtain this equation, consider the change in the total energy E of the region bounded by the fictitious surface D, figure 1, when the system as a whole is subjected to any infinitesimal change whatever, in which equilibrium is preserved. The energy change in question can be due only to (1) the heat absorbed or evolved by the system, (2) the mechanical work done on or by the system through changes in the volumes V^α, V^β and in the area Ω, (3)

[5] The charges $\Delta\theta^\alpha$ and $\Delta\theta^\beta$ added to the two sides of the double layer will by equation 10.1 be equal and opposite. Hence the charges added to the free surfaces of α and β will also be equal and opposite; they will furthermore in general be numerically much smaller than $\Delta\theta^\alpha$, $\Delta\theta^\beta$ because charges of opposite sign tend to come as close together as possible. Therefore, the condition

$$|\Delta\theta^\alpha| = |w_i^\alpha F \Delta n_i^\alpha| = |w_i^\beta F \Delta n_i^\beta| = |\Delta\theta^\beta|$$

will be very nearly fulfilled in most cases.

the change in energy due to changes in the amounts, n_i and n_k of the components X_i and X_k respectively. Consequently

$$dE = TdS - P^\alpha dV^\alpha - P^\beta dV^\beta + \sigma d\Omega + \sum_{i=1}^{p} \eta_i dn_i + \sum_{k=1}^{r} \mu_k dn_k \tag{15}$$

P^α and P^β are the pressures of the phases α and β respectively,[6] σ is the surface tension at the boundary layer B, η_i the electrochemical potential[7] per *equivalent* of X_i, and μ_i the chemical potential per *mole* of X_k, n_i, and n_k being measured in equivalents and moles respectively. Equation 15 contains the general condition for chemical equilibrium, namely, that a particular η_i or μ_k has the same value in all the parts of the system—i.e., both in the homogeneous phase interiors and in the boundary regions—in which the corresponding component is present to an appreciable extent. Since a given X_i is appreciably present in only one of the two phases, each of the η_i refers to only one phase; the same applies to the μ_k of any X_k present in only one of the two phases.

In order to obtain from equation 15 an expression for E^ω, the following relations, all special cases of equation 9, are necessary:

$$dE = dE^\alpha + dE^\beta + dE^\omega \tag{17}$$

$$dS = dS^\alpha + dS^\beta + dS^\omega \tag{18}$$

$$dn_i = dn_i^\alpha + dn_i^\beta + dn_i^\omega \tag{19}$$

$$dn_k = dn_k^\alpha + dn_k^\beta + dn_k^\omega \tag{20}$$

and also the following equations for the energy change that each phase would undergo if it remained homogeneous up to the arbitrary surface C:

$$dE^\alpha = TdS^\alpha - P^\alpha dV^\alpha + \sum_{i=1}^{p} \eta_i dn_i^\alpha + \sum_{k=1}^{r} \mu_k dn_k^\alpha \tag{21}$$

$$dE^\beta = TdS^\alpha - P^\beta dV^\beta + \sum_{i=1}^{p} \eta_i dn_i^\beta + \sum_{k=1}^{r} \mu_k dn_k^\beta \tag{22}$$

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[6] In general, P^α and P^β are related according to

$$P^\alpha - P^\beta = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{16}$$

where r_1, r_2 are the principal radii of curvature of the boundary layer. It follows that in the special case of a plane boundary layer ($r_1 = r_2 = \infty$) represented in figure 1, $P^\alpha = P^\beta$. Equation 15 and the equations deduced from it hold independently of whether the boundary layer is curved or plane, as long as r_1, r_2 are large compared with the thickness of the boundary layer.

[7] The electrochemical potentials η_i play exactly the same rôle for the charged components of a system as the chemical potentials μ_k do for the neutral components; they were first defined by E. A. Guggenheim (J. Phys. Chem. **33**, 842 (1929)). For further discussion of the electrochemical potential, see reference 8.

The substitution of equations 17 to 22 inclusive into equation 15 gives:

$$dE^{\omega} = TdS^{\omega} + \sigma d\Omega + \sum_{i=1}^{p} \eta_i dn_i^{\omega} + \sum_{k=1}^{r} \mu_k dn_k^{\omega} \tag{23}$$

Equation 23 was derived for any change at all in which equilibrium is preserved and hence is generally true. Since the preservation of equilibrium includes that of electroneutrality, the quantities n_i^{ω} in equation 23 cannot all vary independently but only subject to the electroneutrality condition (equation 14.1):

$$\sum_{i=1}^{p} w_i n_i^{\omega} = 0 \tag{14.1}$$

Aside from this restriction, however, the variables n_i^{ω} are all independent, and so are S^{ω}, Ω, n_k^{ω}. The number of independent variables of which E^{ω} is a function is thus $p + r + 1 = J + 1$[8] (cf. equation 6.1).

The simultaneous equations 23 and 14.1 constitute a general thermodynamic solution of the problem of the perfectly polarizable system.

This solution may be obtained in the form of a single equation by solving equation 14.1 for one of the n_i^{ω}, say n_1^{ω}:

$$n_1^{\omega} = -\sum_{i=2}^{p} \frac{w_i}{w_1} n_i^{\omega} \tag{24}$$

and substituting this in equation 23, giving

$$dE^{\omega} = TdS^{\omega} + \sigma d\Omega + \sum_{i=2}^{p} B_i dn_i^{\omega} + \sum_{k=1}^{r} \mu_k dn_k^{\omega} \tag{25}$$

where

$$B_i = \eta_i - \frac{w_i}{w_1} \eta_1 \tag{26}$$

It may be noted that, since the variables whose differentials appear on the right side of the "fundamental equation" (equation 25) are all independent,

$$\left(\frac{\partial E^{\omega}}{\partial S^{\omega}}\right)_{\Omega,\, n_i^{\omega},\, n_k^{\omega}} = T \tag{27.1}$$

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[8] A proof of the theorem that in the perfectly polarizable system any extensive variable G^{ω} is in general a function of $J + 1$ independent variables will be given in a subsequent communication.

$$\left(\frac{\partial E^\omega}{\partial \Omega}\right)_{s^\omega,\, n_i^\omega,\, n_k^\omega} = \sigma \tag{27.2}$$

$$\left(\frac{\partial E^\omega}{\partial n_i^\omega}\right)_{s^\omega,\, \Omega,\, n_{i'}^\omega,\, n_k^\omega} = B_i,\ i = 2, \ldots p \tag{27.3}$$

$$\left(\frac{\partial E^\omega}{\partial n_k^\omega}\right)_{s^\omega,\, \Omega,\, n_i^\omega,\, n_{k'}^\omega} = \mu_k \tag{27.4}$$

where the subscripts $n_{i'}^\omega$ and $n_{k'}^\omega$ mean that all the variables n_i^ω ($i = 2, \ldots p$) and n_k^ω are kept constant except the one with respect to which the differentiation is carried out.

The application of the general equations, 23 and 14.1, or 25, to the problems arising in practice is facilitated by transformation into the Gibbs-Duhem type of equation. The independent variables in equation 25 are all extensive quantities, so that E^ω is a homogeneous function of the first order in these variables. Hence, by Euler's theorem

$$E^\omega = TS^\omega + \sigma\Omega + \sum_{i=2}^{p} B_i n_i^\omega + \sum_{k=1}^{r} \mu_k n_k^\omega \tag{28}$$

Differentiation of equation 28 and subtraction of the result from equation 25 yields the desired relation of the Gibbs-Duhem type:

$$0 = S^\omega \mathrm{d}T + \Omega \mathrm{d}\sigma + \sum_{i=2}^{p} n_i^\omega \mathrm{d}B_i + \sum_{k=1}^{r} n_k^\omega \mathrm{d}\mu_k \tag{29}$$

The most convenient form of this equation is that obtained by solving for $\mathrm{d}\sigma$:

$$\mathrm{d}\sigma = -\, s^\omega \mathrm{d}T - \sum_{i=2}^{p} \Gamma_i \mathrm{d}B_i - \sum_{k=1}^{r} \Gamma_k \mathrm{d}\mu_k \tag{30}$$

in which

$$s^\omega = \frac{S^\omega}{\Omega},\quad \Gamma_i = \frac{n_i^\omega}{\Omega},\quad \Gamma_k = \frac{n_k^\omega}{\Omega} \tag{31.1, 31.2, 31.3}$$

It may be mentioned that of the $p + r + 1 = J + 1$ variables whose differentials appear in equation 30, J are independent[9] if the curvature of the boundary layer is regarded as variable,[10] so that σ may in general be regarded as a function of the J variables T, B_i ($i = 2, \ldots p$), μ_k. The decrease in the number of independent variables from $J + 1$ to J in passing from equation 25 to equation 30 is due to the fact that the variables whose differentials appear in equation 25 are extensive, whereas those whose differentials appear in equation 30 are intensive.

[9] Proof in a subsequent communication.

[10] Cf. footnote [6], p. 121.

Finally, it is to be noted that the substitution of equation 26 into equation 30 shows that just as equation 25 is equivalent to the simultaneous equations 23 and 14.1, so is equation 30 equivalent to the simultaneous equations

$$d\sigma = -s^{\omega}dT - \sum_{i=1}^{p} \Gamma_i d\eta_i - \sum_{k=1}^{r} \Gamma_k d\mu_k \tag{32}$$

$$\sum_{i=1}^{p} w_i \Gamma_i = 0 \tag{14.2}$$

Equation 32 together with the electroneutrality condition in the form of equation 14.2 or 10.2 furnishes the best starting point for the special applications of the theory.

The fundamental equation for E^{ω} having been obtained, it is of course possible to develop the theory of the perfectly polarizable system further along Gibbsian lines, obtaining expressions for the other characteristic functions of the system. This is, however, not particularly necessary, because from the foregoing it is already evident that all the equations will be of the form of the general Gibbsian equations for any boundary layer, with electroneutrality conditions attached, the simultaneous equations obtained by keeping the electroneutrality conditions explicit (e.g. equations 23, 14.1 and equations 32, 14.2) being more symmetrical than the corresponding equations with the electroneutrality conditions implicit (e.g., equations 25 and 30).

6. *Specialization of the general equations*

(1) *Introduction of the physical dividing surface.* The general equations of the perfectly polarizable system have so far been deduced with no special assumptions as to the position of the arbitrary dividing surface C, figure 1, with respect to which the extensive properties G^{ω} and the charge of the double layer are defined. From now on all equations will be limited to the one case of physical interest, mentioned on p. 118, in which the fictitious surface C is placed within the physical barrier C′, characteristic of the perfectly polarizable system. The exact level, $x = x'$ at which C is to be placed within C′ is defined as that in which the following equations, expressing the impermeability of the barrier to charged particles,

$$\epsilon^{\alpha} = F \sum_{i=1}^{p^{\alpha}} w_i^{\alpha} \Gamma_i^{\alpha} \tag{33.1}$$

$$\epsilon^{\beta} = F \sum_{i=1}^{p^{\beta}} w_i^{\beta} \Gamma_i^{\beta} \tag{33.2}$$

are most nearly fulfilled. Γ_i^α, Γ_i^β are the surface densities (in equivalents per unit area) of X_i^α, X_i^β with respect to the level in question, and ϵ^α, ϵ^β are the corresponding charge densities of the double layer.

In order to introduce the condition (equations 33.1 and 33.2) into the general equation (32), it is expedient formally to split up the electrochemical potentials (per equivalent) of the charged components X_i^α, X_i^β as follows:

$$\eta_i^\alpha = \mu_i^\alpha + w_i^\alpha F \varphi^\alpha \tag{34.1}$$

$$\eta_i^\beta = \mu_i^\beta + w_i^\beta F \varphi^\beta \tag{34.2}$$

μ_i^α, μ_i^β are the chemical potentials of X_i^α, X_i^β, and φ^α, φ^β are the absolute electric potentials in the two phase interiors.[11] Writing equation 32 in the form

$$d\sigma = -s^\omega dT - \sum_{i=1}^{p^\alpha} \Gamma_i^\alpha d\eta_i^\alpha - \sum_{i=1}^{p^\beta} \Gamma_i^\beta d\eta_i^\beta - \sum_{k=1}^{r} \Gamma_k d\mu_k \tag{35}$$

and substituting equation 34.1, equation 34.2 gives

$$d\sigma = -s^\omega dT - \sum_{i=1}^{p^\alpha} \Gamma_i^\alpha d\mu_i^\alpha - \sum_{i=1}^{p^\beta} \Gamma_i^\beta d\mu_i^\beta - F \sum_{i=1}^{p^\alpha} w_i^\alpha \Gamma_i^\alpha d\varphi^\alpha - F \sum_{i=1}^{p^\beta} w_i^\beta \Gamma_i^\beta d\varphi^\beta - \sum_{k=1}^{r} \Gamma_k d\mu_k \tag{36}$$

into which equations 33.1 and 33.2 may now be introduced, along with the electroneutrality condition (equation 10.2), giving

$$d\sigma = -s^\omega dT - \sum_{i=1}^{p^\alpha} \Gamma_i^\alpha d\mu_i^\alpha - \sum_{i=1}^{p^\beta} \Gamma_i^\beta d\mu_i^\beta - \sum_{k=1}^{r} \Gamma_k d\mu_k - \epsilon^\alpha d(\varphi^\alpha - \varphi^\beta) \tag{37}$$

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[11] It is to be noted that, as E. A. Guggenheim (J. Phys. Chem. **33**, 842 (1929); **34**, 1540 (1930)) has shown, the quantities μ_i and φ are in general thermodynamically indeterminate. According to Guggenheim, the difference, $\varphi^\alpha - \varphi^\beta$, in electrical potential between two phases is thermodynamically defined only if (i) the two phase interiors are of identical chemical composition, (ii) the two phase interiors consist of ideal solutions in the same solvent, (iii) one or both phase interiors are non-ideal solutions in the same solvent, but the deviations from ideality depend only upon the valence type of the electrolyte components (as in the theory of Debye and Hückel) and are otherwise not specific. *Changes* in $\varphi^\alpha - \varphi^\beta$ are furthermore thermodynamically defined for two phases of *any* composition if the surfaces of the phases are altered without affecting the interiors; this is possible in the perfectly polarizable system (cf. pp. 119 and 120) and also in systems where the two phases can be separated by insoluble films of various sorts (cf. A. Frumkin: Z. physik. Chem. **116**, 485 (1925)).

which is essentially the general equation (30), specialized for the physical dividing surface, $x = x'$, characteristic of the perfectly polarizable system.

(2) *Introduction of the applied potential* $\mathfrak{E}$. Imagine the phase α to be electrically connected with a piece of some arbitrary metal, Me: whether the connection is established by direct contact of α and Me, or alternatively a series of other conducting phases in contact is interposed between α and Me, is immaterial, as long as the absolute potential difference $\Delta\varphi$ across each phase boundary between the interior of α and the interior of Me depends only on the temperature, pressure, and composition of the two phases adjacent to it, i.e., as long as chemical effects and polarization effects are absent. Imagine the phase β to be similarly connected to another piece of the same metal Me. Let φ^{I} denote the absolute electric potential of the Me connected with α, φ^{II} that of the Me connected with β. Then the electromotive force $\mathfrak{E}$ between the two pieces of Me is given by

$$\mathfrak{E} = \varphi^{\mathrm{II}} - \varphi^{\mathrm{I}} \tag{38}$$

$\mathfrak{E}$ may evidently be varied at will by connecting the two pieces of Me to the poles of a potentiometer. If, as will always be the case from now on, α is taken to be the metallic phase, β the nonmetallic phase, then the quantities defined by equation 38 are the abscissas of the electrocapillary curves of the system. $\mathfrak{E}$ may be introduced into equation 37 by writing

$$(\varphi^{\alpha} - \varphi^{\beta}) = (\varphi^{\alpha} - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^{\beta}) - \mathfrak{E} \tag{39}$$

the substitution of which into equation 37 gives

$$\mathrm{d}\sigma = -s^{\alpha}\mathrm{d}T - \sum_{i=1}^{p^{\alpha}} \Gamma_i^{\alpha}\mathrm{d}\mu_i^{\alpha} - \sum_{i=1}^{p^{\beta}} \Gamma_i^{\beta}\mathrm{d}\mu_i^{\beta} - \sum_{k=1}^{r} \Gamma_k\mathrm{d}\mu_k - \epsilon^{\alpha}\mathrm{d}\,[(\varphi^{\alpha} - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^{\beta}) - \mathfrak{E}] \tag{40}$$

This equation is immediately applicable to the problems arising in practice and is to be regarded as the general equation of the electrocapillary curve.

(3) *The Lippmann-Helmholtz equation.* At constant T, P^{α}, P^{β} and composition the quantities μ_i^{α}, μ_i^{β}, μ_k, $\varphi^{\alpha} - \varphi^{\mathrm{I}}$, $\varphi^{\mathrm{II}} - \varphi^{\beta}$ are constant; consequently the differentials of these quantities vanish from equation 40 along with that of T, leaving

$$\left(\frac{\partial\sigma}{\partial\mathfrak{E}}\right)_{T,P^{\alpha},P^{\beta},\text{composition}} = \epsilon^{\alpha} \tag{41}$$

This equation, the so-called Lippmann-Helmholtz equation, is thus shown to depend upon no assumptions save that of perfect polarizability as defined in this paper; it is, therefore, true for any perfectly polarizable system irrespective of composition.

In the determination of an electrocapillary curve by the Lippmann electrometer, the (variable) surface tension σ is measured by observing the (variable) height of a column of mercury (1) necessary to bring the boundary layer between the mercury (or amalgam) and the solution to a fixed position in the capillary of the instrument, the pressure P^β of the solution remaining constant (cf. equation 16). Actually, therefore, P^α is somewhat variable along the electrocapillary curves determined by the Lippmann electrometer, so that equation 41 does not apply rigorously to such curves. The limits of the variation of P^α are, however, small, being always such that (at constant P^β),

$$0 < P^\alpha - P^\beta < 1 \text{ atmosphere} \tag{42}$$

and within these limits the variation of μ_i^α with P^α may without appreciable error be neglected. If the μ_i^α are assumed to be constant, then $\varphi^\alpha - \varphi^{\mathrm{I}}$ is also constant, and since the electrically neutral components are in practice always confined to the solution β, whose pressure P^β remains constant, μ_k, μ_i^β and $\varphi^{\mathrm{II}} - \varphi^\beta$ are constant as before. On the assumption that the variation of the μ_i^α with P^α is negligible, equation 40 therefore gives for the slope of the electrocapillary curves determined by the Lippmann electrometer

$$\left(\frac{\partial\sigma}{\partial\mathfrak{E}}\right)_{T,\, P^\beta,\, \text{composition}} = \epsilon^\alpha \tag{43}$$

Equation 43 is the best known equation concerning electrocapillary curves and has been verified by experiment in various ways (5).

In concluding it may be mentioned that the equation 40 leads directly to the exact equations for the variation of the electrocapillary curve with the composition of the two phases; these equations will be deduced in a subsequent communication.

III. Summary

1. Attention is called to a number of inconsistencies in the existing theory of the electrocapillary curve.

2. These inconsistencies are removed by developing the theory afresh, starting from only one assumption, that of perfect polarizability, which is defined in this paper as meaning impermeability of the boundary layer between two conducting phases to electrically charged particles. This definition is known to correspond closely to the actual physical conditions in the Lippmann electrometer.

3. The general equations resulting from the initial assumption of perfect polarizability are the Gibbsian equations for any boundary layer in equilibrium, with electroneutrality conditions attached.

4. The Lippmann-Helmholtz equation is found to depend upon no

assumptions whatever save the initial one of perfect polarizability; it thus holds for all perfectly polarizable systems regardless of their composition.

The author is indebted to Professor E. Lange, formerly of Munich, now of Erlangen, for calling his attention to some of the difficulties which his paper is an attempt to solve; and to Mr. E. A. Guggenheim, formerly of Copenhagen, at present Visiting Professor in Stanford University, for much valuable aid and advice.

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NEW BOOKS

Flotation. By A. M. GAUDIN. 552 pp.; 145 illustrations; 20 chapters. New York and London: McGraw-Hill Book Co. Inc., 1932. Price: $6.00.

An introduction, written for this book by Dean Theodore J. Hoover, of Stanford University, who wrote the first book on flotation almost twenty-five years ago, states that, "One of the outstanding merits of this book is that it much more fully than any previous attempt gives a practically complete exposition of the scientific principles underlying a process which is treating millions of tons of ore every year."

The author also drew assistance from the other writers of books on flotation, including the present reviewer, who, with the distinguished T. A. Rickard, prepared the second book on flotation about seventeen years ago; the book is dedicated to the author's former teacher, Professor A. F. Taggart, of Columbia University, who prepared the third major treatise in English on flotation at a much more recent date. The result of many suggestions and much criticism before printing has justified Hoover's estimate of the book.

Theory, description, practice, economic effects, are all included. While readers of This Journal are not greatly interested in "Pointers on Mill Design," "Elements of Costs," or "Machinery," there are many chapters on the theory of the process and the technical problems in its application which carry a message.

With rare exceptions the researchers on flotation as a method of ore concentration have not been physical chemists and were inadequately prepared to study a phenomenon which is essentially a problem in physical chemistry. The author himself is not a physical chemist, but has striven faithfully to remedy that defect and has called in the help of many physical chemists, so that his theories might have the background least liable to criticism. The trouble with the periodical literature has been that the physical chemists did not know much about flotation, and the flotation engineers did not know enough physical chemistry. The result has been a flood of near-worthless papers on the theory of the subject.

Gaudin's book goes far toward remedying this defect and starts off with chapters on the following subject: "The Physicochemical Foundations of Flotation," "The Phases in Flotation Systems," "Colloid Systems," "Flotation Reagents," and "The Mechanical Aspects of Froth Production." The physicochemical problem in flotation is first of all to produce a suspension of finely ground ore in water to which is added reagents that will produce froths of the desired consistence and life. Secondly, other reagents must be added which will cause the desired minerals to cling to the bubble interfaces so that they will concentrate in a froth layer or the upper surface of the ore pulp. From a colloid standpoint it is a problem more or less of differential flocculation, attachment of certain classes of mineral particles to bubble surfaces being a function of the degree of flocculation of desired minerals and of gangue minerals. To alter the surface films on particles that normally are not easily floated until they are susceptible of flotation concentration is another problem in physical chemistry.

This book is a good start in the direction of discarding misapprehensions and misapplications of science to a process whose application in industry long ago outdistanced its scientific explanation.

OLIVER C. RALSTON.

Les Sciences Geologiques et la Notion d'État Colloidal. By PIERRE URBAIN. "Actualités Scientifiques et Industrielles, No. 69. Exposés Geochemie. Paris, 1933.

The origin and definition of the term "colloid" are given. The first part of the paper consists of a general discussion of the colloidal state. Colloids are heterogeneous and represent transitions between true solutions and suspensions, and it is impossible to define rigidly the concentration of a colloidal solution. Such a solution is preferably designated as a "pseudo solution." Mixed systems are frequently found, the same substances furnishing crystalline particles, colloidal particles, and dissolved molecules. Silica is cited as an example.

The second part of the paper is concerned with the principal natural colloids. Colloidal phenomena are common in the alteration of minerals near the surface of the earth, but the colloidal form is always transitory and crystalline material is eventually formed. The principal natural colloids are silica, aluminum hydroxide, and iron hydroxide.

Kaolinization is the most universal process in which colloidal minerals are developed. This process attacks the great number of aluminosilicates found in igneous and metamorphic rocks and it frees the alkalies and alkaline earths which then form bicarbonates in superficial waters. Hydrated aluminum silicates are formed and excess silica freed. In laterization the aluminosilicates are destroyed with the elimination of silica and the formation of aluminum and ferric hydroxide. It is suggested that laterization may be due to the decrease in the solubility of carbonic acid with the increase in temperature, since laterites are found mainly in tropical regions. The pH content is important in this connection.

Sodium chloride is an important coagulant of silica in weak solutions; also of clay and limonite where rivers empty into the sea.

The ability of colloids to adsorb plays an important rôle in the elimination of alkalies liberated by the process of kaolinization. Potassium and sodium are present in nearly the same amount in the average rock, but in river and ocean waters sodium is several times as abundant as potassium. This is said to be be due to adsorption of the potassium in preference to sodium. Potassium is favored in the formation of aluminates. Thus potassium is much more abundant than sodium in clays and even in average sedimentary rock. It is concluded that in nature potassium is sixteen times more adsorbable than sodium.

The origin of chalk in the Paris basin is reviewed and the rôle of colloids discussed. Silica and its relation to colloidal processes is briefly discussed. Varieties of silica originally colloidal are opal, chalcedony, and quartz.

Only two varieties of hydrous ferric oxide are recognized, goethite and lepidocrocite, both with the formula $Fe_2O_3 \cdot H_2O$.

The use of the term "metacolloid," suggested by Wherry for microcrystalline minerals originally colloidal, is approved. Lindgren's list of the principal natural amorphous gels and metacolloids is given. Criticisms are given of some of the minerals included and some of those left out and the general significance of the group is discussed. Finally several good microphotographs of rocks of colloidal origin are included in the plates at the end of the paper.

G. M. SCHWARTZ.

Jahrbuch des Forschungs-Instituts der allgemeinen Elektricitätsgesellschaft. Dritter Band, 1931–32. 29.5 x 21.5 cm.; 205 pp. Berlin: Julius Springer, 1933.

The third volume of this important yearbook covers so wide a field that it is impossible to analyze its contents briefly in any connected manner. The simplest way of giving to the readers of This Journal some knowledge of the topics treated is to append a list of the titles of the papers which make up the volume: (1) Die Ent-

wicklung des Tonfilmverfahrens der AEG; (2) Verbesserungen des Zeitdehners und Anwendung in der Aufnahmepraxis; (3) Zur Elektrotechnik der Entladungsgefässe; (4) Zur Physik der Entladungsgefässe; (5) Gaskonzentrierte Elektronenstrahlen und ihre Anwendung; (6) Geometrische Elektronenoptik; (7) Mitarbeit der AEG an der Nordlichtforschung; (8) Untersuchungen uber das Wesen des Elektrons; (9) Wirkung neutrales Gasmoleküle gegenüber langsamen Elektronen und langsamen Protonen; (10) Über die physikalischen Grundlagen der Ionentherapie; (11) Neuartige Werkstoffe für Pupinspulen; (12) Einzelarbeiten des metallurgisch-magnetischen Laboratoriums; (13) Neue magnetische Messmethoden; (14) Beitrage zur Physik der Nitrobenzol Kerrzelle; (15) Über lichtelektrische Alkalizellen.

This table of contents will serve to give some notion of the very varied fare presented, and those interested in any special subject can judge whether any topic of importance to them is discussed in this volume. It is hardly necessary to say that the subjects are handled in a very thorough and interesting fashion, and the volume, both in content and in the matter of mechanical production, is a worthy record of very important work.

ALLAN FERGUSON.

Molecular Rays. By RONALD G. FRASER. xii + 204 pp.; 78 figs. Cambridge University Press. New York: The MacMillan Company.

This book is one of the Cambridge series of physical chemistry under the editorship of E. K. Rideal. The book is of the sort that the English seem to do unusually well, being an account of the technical methods and state of progress in research involving the molecular ray technique. The author spent some time in Stern's laboratory at Hamburg and is qualified by training and experience to write such a manual. He naturally gives a great deal of prominence to the Hamburg laboratory and very properly so, since the molecular ray technique was originated by Professor Stern and its most important applications have been made by him. The consideration given to work along this line in American laboratories is all that could be expected from a book written on the other side of the water. The trend of recent events indicates that molecular ray research may become peculiarly an American institution. The only defect to be noted in the book is the lack of a bibliography.

W. H. RODEBUSH.

Some Physical Properties of the Covalent Link in Chemistry. By NEVIL VINCENT SIDGWICK. 23 x 15 cm.; 249 pp. Ithaca, New York: Cornell University Press, 1933. Price: $2.00.

The volume under consideration is based upon a series of lectures given at Cornell University by the author while he held the George Fisher Baker Non-resident Lectureship during the second semester of 1930–1931.

Owing to the high degree of specialization in chemistry, it is rare to find a chemist who has succeeded in achieving a comprehensive grasp of the science as a whole. Professor Sidgwick is one of the most distinguished of these few. In the present work he has brought together bits of information gathered from the most diverse sources and has interpreted them with reference to their bearing on our conception of the nature of the covalent bond. The result constitutes a classic treatise—the purpose of which is expressed by the author in the following characteristically modest fashion. "The book is an attempt to set out the methods of measurement of some of the more important properties of non-ionized links, and to discuss the results so far obtained." "I have tried to include the more important researches bearing on these questions which have appeared up to the summer of 1932, and a few later ones of special interest."

Following an admirable introductory lecture on the relation of physics to chemistry, the following topics are treated: atomic cohesion; electrovalence and covalence; dimensions of covalent links; heats of formation of covalent links; electrical dipole moments; stereochemistry.

The material presented is of the greatest interest to chemists of every persuasion, and it has been treated in a manner which renders it readily understandable even by those who are not familiar with the original sources from which the work is drawn. The book is highly recommended to all serious students of chemistry.

REYNOLD C. FUSON.

Die Bedeckungstheorie der Passivität der Metalle und ihre experimentelle Begründung. By W. J. MÜLLER. 23 x 16 cm.; 102 pp. Berlin: Verlag Chemie, 1933. Price: paper, 6 marks; bound, 7 marks.

The study of anodic behavior, which has been made by W. J. Müller and his pupils at Vienna over a period of several years, is well-known to all who are interested in the corrosion and passivity of metals. No adequate description of this work exists, other than the large number of experimental papers which have emanated from Müller's laboratory, so that the present book, which describes all the essential matter in a compact form, will be welcomed.

It should be pointed out, however, that the scope of the book is precisely as indicated by the title; that is to say, it is essentially a monograph devoted to the author's own contributions to the subject, and scant mention is made of other views. The book is in no sense a balanced dissertation on passivity, and much work on anodic phenomena which has been carried out by other investigators, and which definitely has a bearing on Müller's work, is passed over with a mere reference.

After demonstrating Müller's most striking contribution to the subject—that anodic passivity is a time phenomenon—the author formulates equations which represent the laws of sideways-growth and thickening of the film, relates these to specific anodic systems, and incidentally uses the results to explain the rectifying action of the aluminum electrode.

The book is well illustrated with photomicrographs and diagrams and can be commended as a valuable addition to the literature on passivity.

E. S. HEDGES.

Infra-red Photography. By S. O. RAWLING. 13 x 19 cm.; x + 57 pp. London: Blackie and Son, Limited, 1933. Price: 3s. 6d.

The recent introduction of easily handled infra-red plates by the leading manufacturers of photographic materials has rendered possible the application of infra-red photography to long distance and aerial photography, chemical record work, detection of forgery, photomicrography, and spectroscopy. The author has written an admirably clear account of the handling and applications of the new commercial plates. The chapters which deal with the choice of suitable safelights, light filters, lenses, and photographic apparatus should be carefully read by all who use, or intend to use, infra-red photography for any purpose whatever. In particular it will surprise most photographers to learn that leather camera bellows and the various woods used in the construction of dark-slides may transmit sufficient infra-red radiation to cause fogging of the sensitive material.

The value of the book is enhanced by the inclusion of a number of excellently reproduced photographs.

EDWIN E. JELLEY.

THE ELECTROKINETIC (ZETA) POTENTIAL OF THIN METAL FILMS[1]

GRANT W. SMITH AND L. H. REYERSON

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received September 6, 1933

One of the problems in the study of the electrokinetic potential has been the proof that the potentials as measured are different from the thermodynamic potentials of Nernst. The development of the glass electrode by Haber and Klemensiewicz enabled investigators to compare the potentials of this electrode in various solutions of electrolytes with the potentials obtained by streaming the same solutions through glass capillaries made from the same glass as the glass electrode. Measurements of this kind have shown a real difference in the values of the potential as measured by the two methods. The glass electrode behaved essentially as a hydrogen electrode, while the measurements of potentials by streaming solutions through glass capillaries showed that these potentials were sensitive to small changes in ion concentrations, especially if the ions were polyvalent. In addition it has been shown that the glass electrode is far from a simple system. As a result it is doubtful whether a real comparison can be made between the two potentials by the use of glass. The desirability and importance of finding a simple metal–solution system for streaming potential study becomes clearly evident.

Previous work in this laboratory has shown that silica gel could be metallized so that the extensive surface of the gel was well covered by a metal deposit. The evidence further showed that metal layers could be made thick enough to show the crystal structure of the metal in x-ray studies. Accordingly it was felt that such metallized gels might be used in streaming potential measurements and that a direct comparison with the thermodynamic potential thus could be obtained. The gel itself would act as an insulator having the metal film on it. In the following investigation, streaming potential measurements are reported for nickel and silver surfaces in solutions containing the ions of the metals used. These metals were chosen so as to have one metal above and the other below hydrogen in the electromotive force series. The results on two such metals would

[1] The material here presented formed a part of a thesis submitted to the graduate faculty of the University of Minnesota by Grant W. Smith in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1932.

more nearly answer the question of the similarity or dissimilarity of the two potentials.

EXPERIMENTAL PROCEDURE

The metallized silica gels were prepared by allowing a purified silica gel to adsorb the complex ammonia ions of silver, $Ag(NH_3)_2^+$, or of nickel, $Ni(NH_3)_4^{++}$, from an aqueous solution. Silica gel adsorbs these cations very strongly, 1 g. of silica gel adsorbing as much as 0.32 g. (1.692 millimoles) of the silver complex and 0.31 g. (1.10 millimoles) of the nickel complex.[2] After adsorption had reached equilibrium the liquid was drained from the gel, the gel was dried, and finally heated in a current of hydrogen until the complex salt in the gel was reduced and the metal left in a free state on the surface of the gel. The product was a deep black, and microscopic examination of the granule showed no uncovered silica surfaces.

In order to make sure that the metallized gels were sufficiently coated, they were analyzed by means of x-rays. Using copper radiation, definite patterns of the metals deposited on the gel were obtained. Silver wire and nickel wire produced patterns which were identical with those of the corresponding powdered gels. The lines of the nickel gel were faint but definite. Both gels gave broader lines than the metal wire, indicating that the metallic film was very thin and of approximately colloidal dimensions.

The apparatus used in this investigation consisted of three essential parts: a diaphragm of finely divided material packed between two perforated electrodes, with a system for forcing the liquid through the diaphragm under known hydrostatic pressures; a potentiometric device for measuring the E.M.F. developed between the two electrodes; and a conductivity bridge.

The streaming potential cell was of the same general type as that used by Briggs, except that some of the dimensions were altered to suit the particular case at hand. The ring in which the diaphragm material was packed was made of clear Bakelite, furnished by the Bakelite Corporation. Its outside diameter was 4.5 cm.; its inside diameter, 3.5 cm. It was 2.5 cm. in width. The two electrodes were made to fit on either side of the ring. They were of 14 K gold, 4.5 cm. in diameter and 1 mm. thick. The electrodes were perforated with 0.5 mm. holes to within 0.5 cm. of the circumference, the holes lying as closely together as they could be drilled without weakening the electrodes too much. A platinum wire was soldered with gold solder to the edge of each electrode to form a connection with the electrical measuring instruments. The two flared tubes which formed the rest of the cell were made of Pyrex glass. The cell was assembled with thin rubber gaskets to insure against leaks, and the whole was clamped tightly together with a specially constructed clamp.

[2] Unpublished results of a series of similar experiments in this laboratory confirm the strong adsorption of complex ammonia ions in ammoniacal solution.

Figure 1 shows the complete cell and pressure system. Z is the zeta potential cell which has just been described. M is a mercury manometer by which pressures up to about 80 cm. can be read. N is a cylinder of nitrogen which was used to supply the pressure on the streaming liquid; V is a reducing valve for controlling the pressure. S_1, S_2, S_3, and S_4 are stopcocks, and A_1 is a "valve" controlled by a screw clamp. F_1 is a 5-liter Pyrex flask in which the liquid which is to be streamed through the cell is placed. It is fitted with a three-hole stopper through which go the inlet tube from the pressure line, the outlet tube to the cell, and a closed-end glass tube holding a piece of ruled paper for measuring the water level. E is a clamp. F_2 is another 5-liter flask which is used to catch the waste liquid

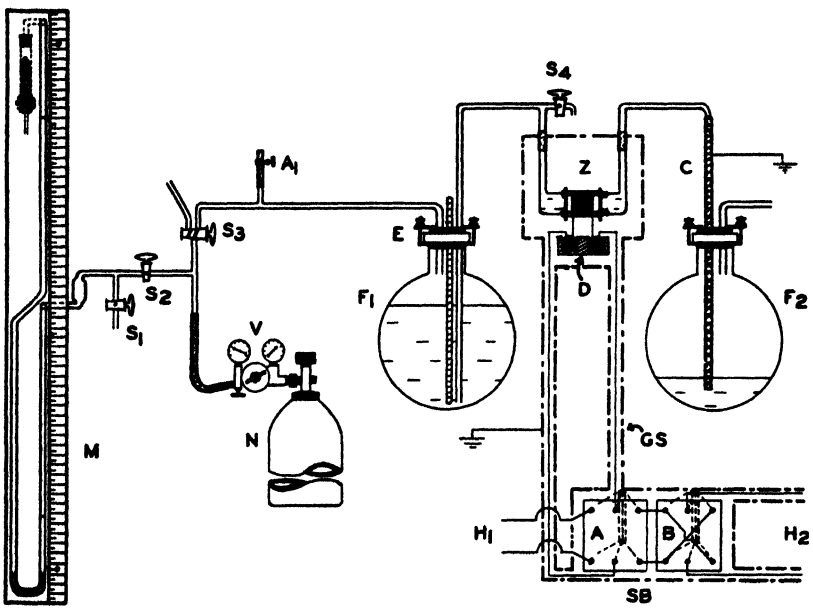

FIG. 1. THE COMPLETE CELL AND PRESSURE SYSTEM

from the cell. C is a piece of flexible metal tubing which is grounded, and is used to carry off the waste liquid after it has streamed through the cell. This was found to be necessary, for the flow of liquid down a glass tube caused very disturbing electrical effects. D is a sulfur block holding two mercury cups in which dip the leads from the cell and from the measuring instruments. A and B are "rocker" switches, consisting of mercury cups set in sulfur blocks. B is a reversing switch which reverses the direction of the E.M.F. of the cell with reference to the potentiometer in the circuit. When A is to the left, the cell is in the circuit of the conductivity bridge; when it is to the right, the cell is in the potentiometer circuit. H_1 shows the leads to the bridge, while H_2 shows those to the potentiometer. GS is

grounded shielding about the leads from the cell, the cell itself, and the switches, A and B. The shielding about the lead wires consists of 1½ inch brass tubing. The cell is shielded with copper gauze. The switches are in a copper switch box, SB, made of copper sheeting.

It was originally intended to use a quadrant electrometer as the null instrument in the measurement of the E.M.F. of the cell, but vibrations in the room used for this investigation made it impossible. Several cushion and suspension mountings were tried without avail. A vacuum tube potentiometer was then built for the purpose. The circuit used was much

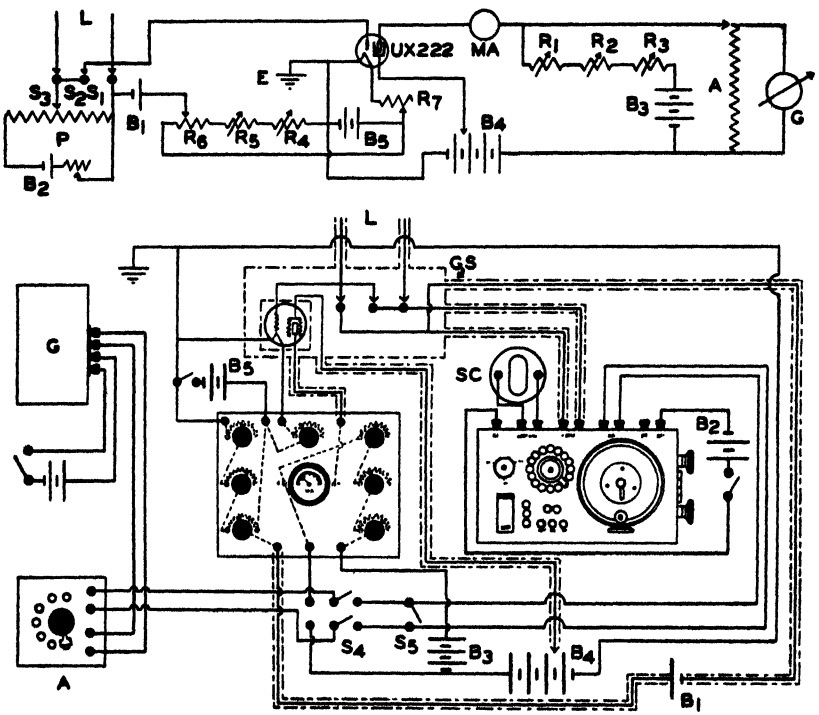

FIG. 2. THE ELECTRICAL CIRCUIT AND THE WIRING DIAGRAM

the same as described by Fosbinder (4) (see also Nottingham (6)). The set-up as constructed employs a potentiometer as a null instrument, and a screen grid vacuum tube as amplifier. It draws only a negligible amount of current from the cell during adjustment and no current at all at the balance point. Furthermore it is not affected by ordinary mechanical vibrations.

Figure 2 gives both the electrical circuit and the wiring diagram. The principle of operation is as follows: With the grid circuit open, the plate current through a sensitive galvanometer (G) is adjusted by means of a

shunt resistance and battery (R_1, R_2, R_3, and B_3) until there is no galvanometer deflection. Now the grid circuit is closed by means of a switch (S_1), and adjusted by a shunted resistance and battery (R_4, R_5, R_6, and B_5) until there is again no deflection on the galvanometer in the plate circuit. This adjustment has brought the grid to the same potential it was at when the grid was open, i.e., at "floating potential," as it is sometimes called. The switch (S_1) is now opened, and another switch (S_3) is closed, which brings the cell and the potentiometer into the grid circuit. The potentiometer is now balanced against the cell in the usual manner, until there is again no galvanometer deflection, and the reading on the potentiometer is the potential difference across the cell. No current is drawn from the cell at the balance point, for the grid is always at "floating potential" just as though it were an open circuit, i.e., as though the resistance of the grid circuit were "infinite" as it was when the first adjustment was made.

The vacuum tube is of the screen grid type, UX 222. MA is a milliameter with a full scale deflection of 1.5 milliamperes; during use this reads about 0.5 milliampere. R_1, R_2, and R_3 are radio rheostats with resistances of 10,000 ohms, 5,000 ohms, and 100 ohms, respectively. R_4 and R_5 are 6-ohm and 100-ohm rheostats, and R_7 is a 30-ohm rheostat. R_6 is a radio potentiometer of 2000 ohms resistance. B_1 is an ordinary dry cell. B_2 is the potentiometer battery, two dry cells in series. B_3 is a 4.5-volt battery composed of nine dry cells in series-parallel. B_4 is the plate battery, two heavy duty 45-volt "B" batteries. B_5 is a lead storage battery of 6 volts. A is a Leeds and Northrup 40,000 ohm Ayrton shunt. G is a Leeds and Northrup #2420c galvanometer. L indicates the leads to the zeta potential cell (see H_2, figure 1). P is a Leeds and Northrup Type K potentiometer. S_1, S_2, and S_3 are specially constructed switches of small electrical capacities. SC is a Leeds and Northrup Weston standard cell, #7307. S_4 is a double throw double pole switch by means of which the galvanometer may be brought into the Type K potentiometer circuit so that the latter may be checked with the standard cell, or into the vacuum tube plate circuit. When S_4 is in the latter position, S_5 must be closed to short the galvanometer connections on the Type K potentiometer. GS is grounded shielding, indicated throughout the wiring diagram by broken lines. The wire leads are shielded with metal tubing. The switches, S_1, S_2, and S_3 are enclosed with the vacuum tube in a large copper box, and are controlled from outside conveniently by means of threads which run over pulleys to some little distance from the box. The vacuum tube is mounted on a cast sulfur base, inside a small copper box which is suspended by rubber bands in the larger copper box which also encloses the switches mentioned above. It was found necessary to shield all vital parts carefully, as shown in the diagram. The whole apparatus was shielded as completely as was practical by building a large "cage" of copper gauze about

it. The potentiometer was found to be very satisfactory in this work, being unaffected by vibration in the building. It proved to be very sensitive also, for a change of 0.0001 volt on the potentiometer from the balance point was easily detected on the galvanometer.

Figure 3 shows the conductivity bridge. The arrangement is adapted from the Wheatstone bridge circuit used by Jones and Josephs (5). The apparatus was modified in several particulars, but the working principle is the same. The oscillator is shown at O; it is a vacuum tube oscillator, and although it was constructed so that it created little external field, it was

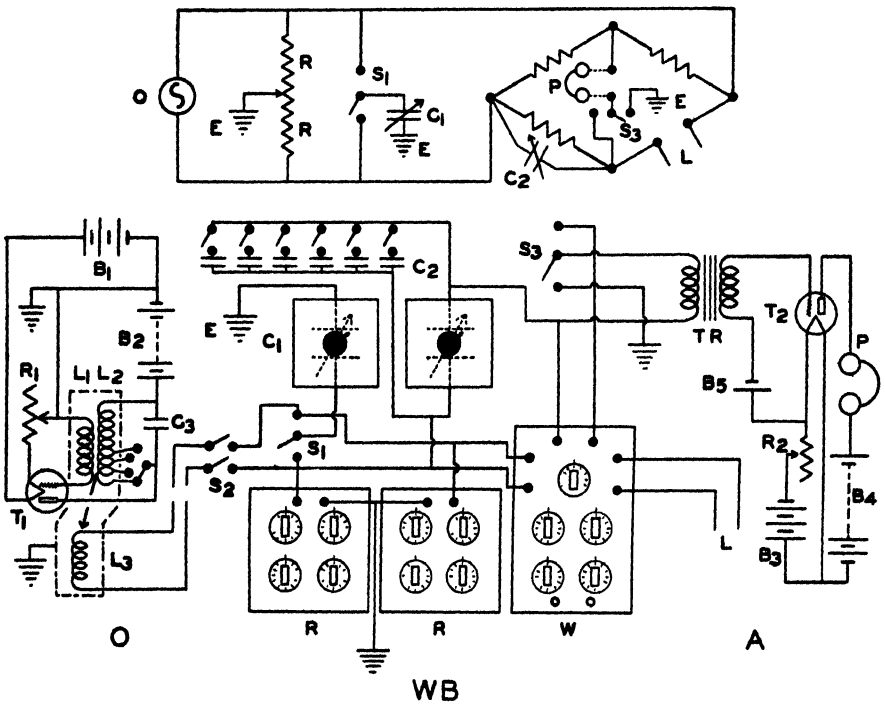

FIG. 3. THE CONDUCTIVITY BRIDGE

placed at a distance of about ten feet from the rest of the apparatus. T_1 is a "power tube," UX 171 A. B_1 is the filament battery, a 6-volt storage or Edison battery. B_2 is a "B" battery of 67.5 volts. L_1, L_2, and L_3 are the grid, plate, and output coils, respectively. They are wound about an iron core, with #30 B & S gauge enameled wire, and mounted in a copper box to shield them from the rest of the apparatus. The plate coil, L_2, is tapped in four places, and by means of the multiple switch shown in the diagram the pitch of the sound may be varied readily. C_3 is a fixed condenser of 0.11 microfarad capacity, found suitable by trial.

A vacuum tube amplifier is shown at A. T_2 is a UX 201 A tube. B_3 is a 6-volt storage battery; B_4 is a "B" battery of 90 volts. P is a set of phones. TR is an audio transformer of four to one ratio.

The Wheatstone bridge itself is at WB. W is a Wheatstone bridge of the dial type, equipped with a multiplier. R and R are variable resistances of 10,000 ohms each. C_1 is a variable condenser of 0.0005 microfarad capacity. C_2 is a variable capacity consisting of seven condensers in parallel: a variable capacity of 0.0005 microfarad, and six fixed condensers of respective capacities, 0.0005, 0.001, 0.002, 0.002, 0.004, and 0.1 microfarad, so that any desirable values from 0.0 to 0.02 microfarad may be obtained by manipulating the switches properly. S_3 is a switch used to connect the phones either to earth or to the bridge, as shown. L indicates the leads to the cell (see H_1, figure 1). The operation of the bridge is as follows: With S_3 in position so that the phones are in the bridge circuit, the bridge, W, and the capacity, C_2, are adjusted so that the sound is as near a minimum as possible; S_3 is then thrown to the other position, grounding the phones, and the resistances, R, R, and the condenser, C_1, are adjusted until the sound is again a minimum. This adjustment brings the phones to earth potential. Now S_3 is put back in its original position, and W and C_2 further adjusted until a minimum is reached. If the position of W is much different from its former setting, the process should be repeated. In this manner, a very distinct minimum point is obtained. The two points on the bridge (see upper diagram) which are joined to the phones are now both at earth potential, and noises which are due to the difference in potential between the phones and the earth are eliminated. In fact, in the operation of this conductivity bridge, a point of dead silence was practically always obtained at a very sharply defined dial position on W. The resistance can be determined accurately to four figures, and the multipliers on W can be used for very large or very small resistances.

The water which was used for streaming through the cell and for making all solutions was conductivity water which was reboiled just before use. Its specific conductivity at room temperature ranged between 0.9×10^{-6} and 1.6×10^{-6} mhos, and was generally about 1.1×10^{-6} mhos. Mallinckrodt's "Reagent Quality" nickel nitrate and silver nitrate were used without further purification for making up the streaming solutions. Since from three to five liters of solution were prepared for each streaming potential run, they could be made up with considerable accuracy even though the concentrations were only fractions of millimoles per liter. The volumetric apparatus and the weights used to weigh the salts were calibrated. The greatest care was exercised at all times to prevent contamination of the water and solutions while handling, and the air over the liquids was displaced by nitrogen from the pressure tank (N, figure 1) as soon as they were placed in the apparatus in preparation for a run.

The diaphragm was prepared in the following manner. The diaphragm material, i.e., the silica gel, was ground in an agate mortar and separated by screening into four groups according to size, (1) larger than 28 mesh, (2) between 28 and 65 mesh, (3) between 65 and 200 mesh, and (4) smaller than 200 mesh. The diaphragm was made up almost entirely of the finest material (4). The coarser gels were used only to fill in the holes in the electrodes so that the finely powdered material would not be washed away when the liquid was forced through the cell. That is, right next to the electrodes on either side, was, first, a thin layer of the coarsest gel, followed by a thin layer of the next size, and then a layer of the next finest gel. With the holes well stopped in this manner, the rest of the diaphragm was made up with the gel of finest particle size. This was kept moist with pure water and packed very tightly.

METHOD OF MAKING A RUN

The cell was now assembled in place as shown in figure 1. The water or aqueous solution was put into the reservoir flask (figure 1, F_1) and the air above it displaced by nitrogen. By applying pressure, the liquid was then streamed through the cell at a very slow rate for at least twenty-four hours before any readings were taken. It was found that about this length of time was required for the diaphragm and liquid to reach equilibrium. If too short a time were allowed for this operation, reproducible stream potentials could not be obtained. It is to be noted that, owing to the porous nature of the diaphragm materials, a considerably longer time was required for equilibrium conditions to be set up than would be the case with such materials as glass, quartz, cellulose, and other substances which have been used hitherto in streaming potential work.

About twenty minutes were required for the potentiometer to reach a steady state so that readings could be made. The liquid was streamed through at a given pressure until at least three consecutive readings in good agreement were obtained over a period of several minutes. Immediately after measurement of the E M.F. the mercury manometer was read, the difference in level between the liquid in the reservoir and the liquid leaving the cell was taken (pressure correction), the temperature read, and the conductivity was measured by switching the cell over to the bridge circuit. The pressure was then changed and the process repeated. The potentiometer was frequently checked with the Weston standard cell. Since the laboratory in which this work was done was an inner room, the temperature was quite constant, and was always near 25°C.

After all of the desired runs were made upon any one diaphragm, the cell constant was determined by streaming a standard $N/50$ potassium chloride solution through it until a constant resistance was reached. The specific conductivity of the liquid in the diaphragm could then be calculated for each run.

RESULTS

The values of the electrokinetic (zeta) potential are calculated according to the expression used by Briggs (1),

$$\zeta = \frac{4\pi\eta H\kappa_s}{P\epsilon} \tag{1}$$

where H is the electromotive force set up across the diaphragm, κ_s is the specific conductivity of the liquid in the diaphragm, η the viscosity of the solutions, P the hydrostatic pressure, and ϵ the dielectric constant. Using the proper constants at 25°C.,

$$\zeta(\text{volts}) = 97.165 \times \frac{H\kappa_s}{P} \tag{2}$$

where H is measured in millivolts, κ_s in reciprocal ohms, and P in centimeters of mercury. Bull and Gortner (2) suggest, in view of the existing doubt as to the correct value of the dielectric constant which should be used in the formula, that the value of the electric moment of the double layer be used to express the capillary electric conditions at the interface instead of the electrokinetic potential. The electric moment of the double layer is equal to the charge per unit area multiplied by the distance between the layers. This expression was met in the derivation of the formula for the streaming potential. It is

$$qd = \frac{\zeta\epsilon}{4\pi} \tag{3}$$

If the value of ζ from equation 1 be substituted in equation 3 we obtain the following expression for the electric moment

$$qd = \mu = \frac{\eta\kappa_s H}{P} \tag{4}$$

Thus the value of the dielectric constant has been eliminated from the calculation. In the tables given in the following sections the values of ζ are negative unless otherwise indicated. The value of the electric moment μ was also calculated and included in the results. The negative value of ζ means that the fixed wall bears a negative charge with reference to the movable liquid layer.

In the preliminary measurements purified silica gel was used for the diaphragms. The H/P ratio was found to be constant at pressures above about 25 cm., but the values fell at lower pressures. Bull and Gortner (3) ascribe a similar result on their quartz diaphragms to a difference in the size of the particles composing the diaphragm. In the present case the fall in H/P values in the low pressure range may be attributed logically to the

porous character of the material, rather than to variations in particle size. It was found that gels prepared under different conditions gave different potential values, so that samples of the same gel were used throughout the entire investigation. Table 1 gives a typical set of determinations on pure silica gel.

TABLE 1

ζ-Potential of water–silica gel

t = 24.9°C. Average κ_s = 2.04×10^{-5}

P	H	H/P	ζ
cm. Hg	*mv.*		*mv*
72.6	153 8	2.12	4 2
53.4	115 2	2.16	4 3
52.0	112 0	2.15	4.3
58.9	125 5	2.13	4.2
48.5	103.8	2.14	4.2
37.3	78.5	2.11	4.2
22.0	48.5	1 97	3.9
11.6	17.7	1.53	(3.0)
12.3	18 9	1 54	(3.0)

TABLE 2

ζ-Potential of water–nickel

t = 24.8°C. Average κ_s = 2.6×10^{-5}

P	H	H/P	ζ
cm. Hg	*mv*		*mv.*
47.2	110.0	2.33	6.0
69.6	172.8	2.48	6.3
69.3	172.7	2.49	6 3
55.5	134.0	2.41	6.2
54.9	132.0	2 40	6.1
30.4	67.7	2.22	5.7
29.7	65 9	2.22	5.7
18.1	37.6	2.08	(5.3)
38 6	88 9	2.30	5.9
Average.....			6.0

TABLE 3

ζ-Potential of N/10,000 nickel nitrate–nickel

t = 25.4°C. $\kappa_s = 4.47 \times 10^{-5}$

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
48.7	74.8	1.54	6.6
47.9	72 8	1 52	6.6
65.8	95.6	1 45	6 3
65.6	95.2	1 45	6.3
75.5	113 0	1.50	6 5
Average.....			6 5

TABLE 4

ζ-Potential of N/5000 nickel nitrate–nickel

t = 25.4°C. Average κ_s = 5.09×10^{-5}

P	H	H/P	ζ
cm. Hg	*mv*		*mv.*
49 3	58 4	1.19	5.9
73.5	86.4	1.18	5.8
72.9	85.0	1.17	5 8
52 0	61.4	1.18	5.8
63.9	74.2	1.16	5.7
34 5	41.6	1.20	5.9
25.8	31.4	1.21	6.0 (over)
Average.....			5.9

Following the preliminary determinations of the electrokinetic potentials of water–silica gel, it was decided to limit the present investigation to the study of gels metallized with nickel and with silver. This gives one metal above and one below hydrogen in the E.M.F. series.

Tables 2, 3, 4, 5, and 6 give the results of electrokinetic potential measurements on nickel-coated silica gel in pure water, $N/10{,}000$ nickel nitrate, $N/5000$ nickel nitrate, $N/2000$ nickel nitrate, and $N/1000$ nickel nitrate solutions, respectively.

Figure 4 shows these results graphically and compares the electrokinetic potential with the Nernst potentials for the same concentrations of Ni^{++}. The full curve gives the character of the change of the ζ-potential with

TABLE 5

ζ-Potential of N/2000 nickel nitrate–nickel

t = 24.4°C. Average κ_s = 1.14×10^{-4}

P	H	H/P	ζ
cm. Hg	*mv*		*mv*
59.7	0.0	0 0	0.0
73 8	0 0	0.0	0 0
73.5	0 0	0 0	0 0
41.5	0.0	0 0	0.0
40.7	0 0	0 0	0 0
Average			0 0

TABLE 6

ζ-Potential of N/1000 nickel nitrate–nickel

t = 25.0°C. Average κ_s = 1.71×10^{-4}

P	H	H/P	ζ
cm. Hg	*mv*		*mv.*
36.6	0.0	0.0	0.0
75.7	0 0	0.0	0.0
74 7	0.0	0 0	0.0
46.7	0.0	0 0	0 0
32 0	0.0	0 0	0 0
Average			0.0

TABLE 7

ζ-Potential of N/10,000 silver nitrate–silver

t = 26.2°C. Average κ_s = 2.32×10^{-4}

P	H	H/P	ζ
cm. Hg	*mv.*		*mv*
58.2	8.6	0.148	3.3
73.6	14.9	0 202	4.5
73.4	14.5	0 197	4.3
63.6	10.5	0.165	3.6
46.4	3.7	0.079	1.7

TABLE 8

ζ-Potential of water–silver

t = 25.2°C. Average κ_s = 4.88×10^{-5}

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
75.4	112.9	1.50	7.3
66.0	101.3	1 53	7.2
57.4	95.6	1.66	7.8
41.0	70.1	1.71	8.0
53.9	86.4	1.60	7.5
Average			7.6

concentration, while the broken line shows the ϵ-potential values through a like change in concentration. In order to get both curves on the same figure, it was necessary to use a different scale for plotting the two potentials. This is indicated on the margin in figure 4.

Following the work on the nickel-coated gels, a series of measurements were carried out on the silver-coated gel. Table 7 gives a typical set of results. It was apparent that the silver gels were not giving uniform

results. Figure 5 shows the dependence of H on the pressure for three solutions of silver nitrate as well as for pure water. The values given in table 7 are shown as No. II in figure 5. Theoretically the curves in the pressure–potential diagram should be straight lines passing through the origin.

The curve No. I for water is the only one that passes through the origin. It appears as though some positive potential were being superimposed on the negative streaming potentials. This is approximately given by the intercept of the extended curves on the ordinate. If this is corrected for by

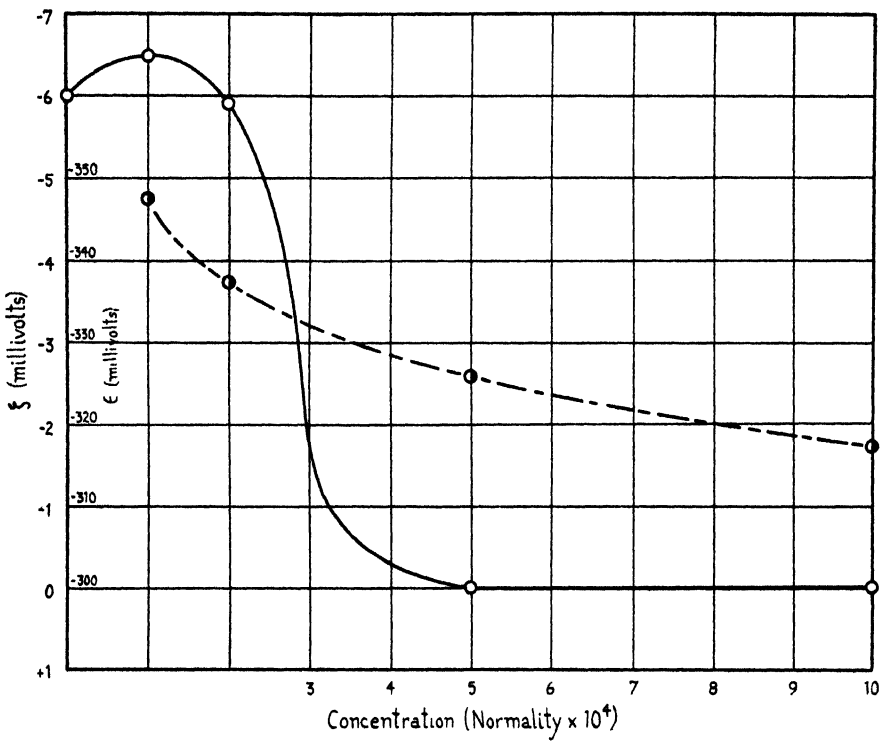

FIG. 4. NICKEL–NICKEL NITRATE

moving the curves parallel to themselves until they pass through the origin, then the values seem reasonable as shown in figure 6. Here the curves of figure 5 have been moved parallel to themselves until they passed through the origin. An additional set of values for $N/1000$ silver nitrate has been added.

The anomalous behavior of the silver gels was early shown to be due to other factors than the silver ions. Measurements of the streaming potentials for dilute silver nitrate solutions on pure silica gel gave uniform results. It was then suspected that the silver gels might be acting as an

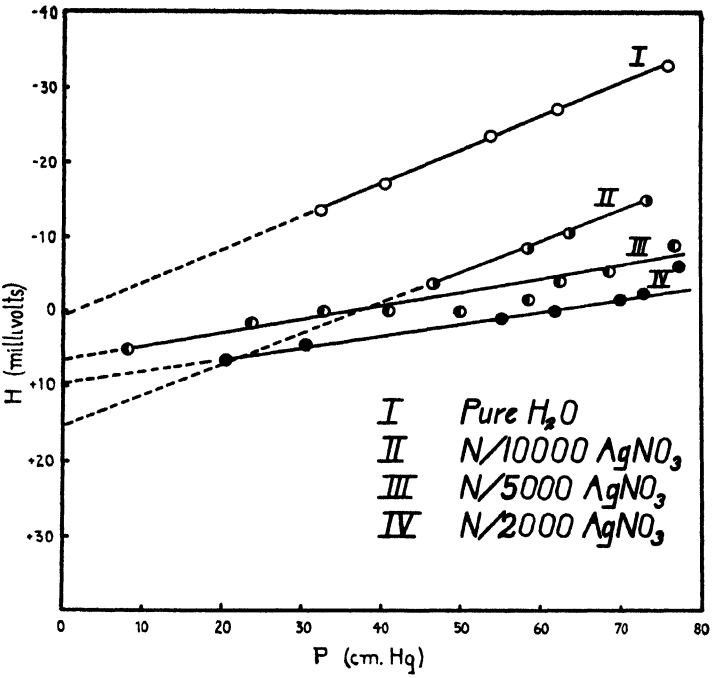

FIG. 5. ABNORMAL SILVER-SILVER NITRATE CURVES

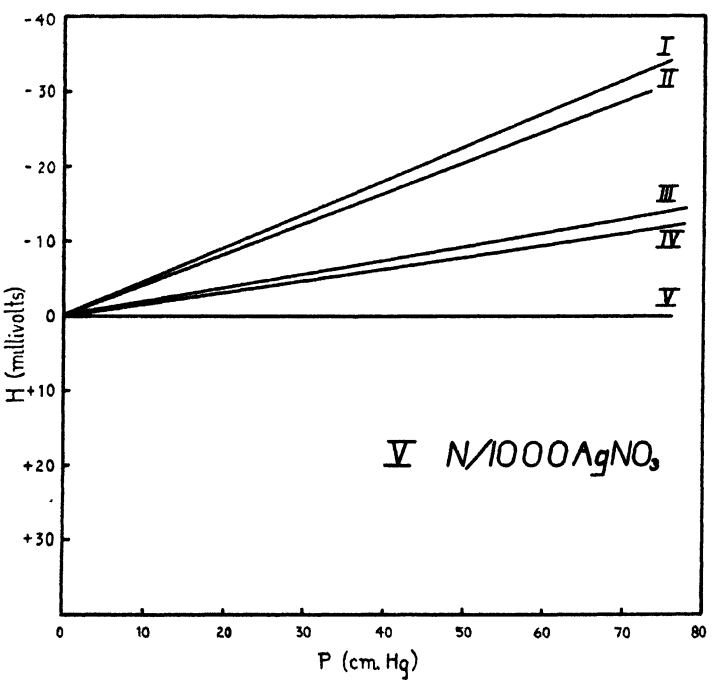

FIG. 6. CURVES FROM FIG. 5 MOVED TO A COMMON ORIGIN

oxygen electrode. A sample of the silvered gel was ground and resilvered. Every precaution was taken to keep oxygen from the gel or the solutions used. The solutions were prepared and stored under nitrogen. The silvered gel was kept in a hydrogen atmosphere until used. The streaming potential results on these gels gave the same anomalous results. In fact

TABLE 9

ζ-Potential of N/10,000 silver nitrate–silver

t = 25.5°C. Average κ_s = 8.98×10^{-5}

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
70.6	42.4	0.600	5.2
77.1	44.4	0.575	5.0
63.7	35.6	0.560	4.8
46.3	24.0	0.519	4.5
59.0	32.4	0.549	4.8
Average.....			4.9

TABLE 10

ζ-Potential of N/5000 silver nitrate–silver

t = 25.8°C. Average κ_s = 1.17×10^{-4}

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
74 5	39.3	0.528	5.9
70.1	36.6	0.522	5.9
43.1	21.3	0.495	5.5
56 4	27.9	0.494	5.5
Average.....			5.7

TABLE 11

ζ-Potential of N/2000 silver nitrate–silver

t = 25.9°C. Average κ_s = 1.67×10^{-4}

P	H	H/P	ζ
cm. Hg	*mv.*		*mv*
77.8	22.6	0.290	4.6
66.4	18.1	0.272	4.3
43.3	12.0	0.277	4.4
63.2	16.5	0.261	4.2
51.9	14.5	0.279	4.4
70.3	18.2	0.259	4.2
(00.0)	(00.0)	(0.000)	(0.0)
52.9	15.2	0.287	4.6
Average.....			4.4

TABLE 12

ζ-Potential of N/1000 silver nitrate–silver

t = 25.3°C. Average κ_s = 2.27×10^{-4}

P	H	H/P	ζ
cm. Hg	*mv.*		*mv.*
64.1	8.0	0.124	2.7
76.1	9.6	0.126	2.8
49.9	7.2	0.143	3.1
36.5	4.7	0.129	2.8
60 2	7.8	0.130	2.9
Average.....			2.9

at the end of a run using $N/2000$ silver nitrate, a positive potential was registered after the pressure on the flowing liquid was brought to zero. This potential persisted for more than an hour after the liquid had ceased to flow.

Since the metallized gels were reduced and stored in an atmosphere of hydrogen it was felt that there might be some hydrogen electrode effect,

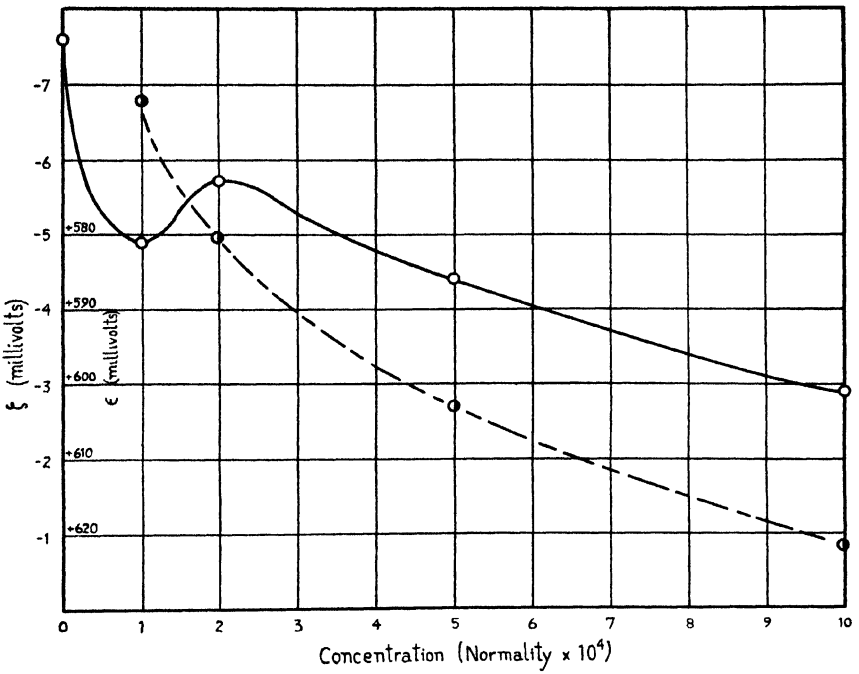

FIG. 7. SILVER–SILVER NITRATE

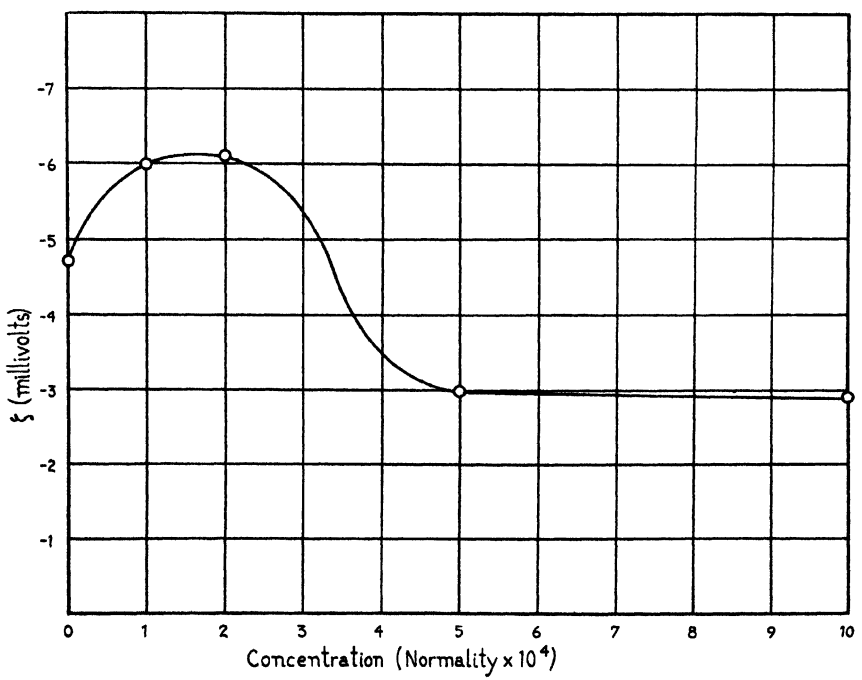

FIG. 8. SILICA GEL–SILVER NITRATE

since oxygen had been eliminated from the system. Accordingly a fresh sample of silvered gel was prepared as previously described. This was placed in bulbs and sealed to a vacuum line. The bulbs were heated for two hours at a temperature above 350°C. while the vacuum pump was running. The bulbs were sealed off under vacuum and later opened under freshly boiled water. As a result a diaphragm of silverized gel was prepared under conditions which practically eliminated both oxygen and hydrogen from the system. A series of measurements were made on this gel and the results are given in tables 8, 9, 10, 11, and 12. These results

TABLE 13

Summary of results for the systems nickel–nickel nitrate

CONCENTRATION	ζ	μ
normality	*mv*	*e.s.u.* $\times 10^{18}$
0×10^{-4}	6 0	11.2
1×10^{-4}	6.5	12.1
2×10^{-4}	5 9	11.0
5×10^{-4}	0.0	0.0
10×10^{-4}	0 0	0.0

TABLE 14

Summary of results for the system silver–silver nitrate

CONCENTRATION	ζ	μ
normality	*mv*	*e s.u.* $\times 10^{18}$
0×10^{-4}	7.6	14.1
1×10^{-4}	4.9	9.1
2×10^{-4}	5.7	10.6
5×10^{-4}	4 4	8.2
10×10^{-4}	2.9	5.4

TABLE 15

Summary of results for the system silica gel–silver nitrate

CONCENTRATION	ζ	μ
normality	*mv.*	*e.s.u.* $\times 10^{18}$
0×10^{-4}	4.7	8.7
1×10^{-4}	6.0	11.1
2×10^{-4}	6 1	11.3
5×10^{-4}	3.0	5.6
10×10^{-4}	2.9	5.4

show that the disturbing influence was eliminated by the above treatment. Figure 7 graphically shows the effect of the concentration of silver nitrate on the zeta potential. As in figure 4 the broken curve shows the change of the Nernst potential with concentration. The values of the Nernst potential in both cases are those referred to the standard hydrogen electrode.

The results of a similar series of determinations on pure silica gel, using silver nitrate solutions, are shown graphically in figure 8.

A summary of the results obtained on nickel-surfaced gel, silver-surfaced gel, and pure silica gel is given in tables 13, 14, and 15. The last column gives the values of the electric moment of the double layer.

DISCUSSION

The streaming potential measurements in this investigation plainly indicate the difference in character between the ϵ and ζ potentials. The electrokinetic potential is negative for both the nickel and silver systems, while the silver–silver ion system would normally be expected to be positive. The actual change in the electrokinetic potential is usually small as compared to the ϵ-potential changes in the same concentration range, but the relative change in the zeta potential is much larger. The zeta potential in the nickel–nickel nitrate system reached a zero value at a concentration of $N/2000$. This is characteristic of the effect of divalent ions in streaming potential studies. No such results are found in ϵ-potentials. The curve obtained for silver nitrate–silver is different from any hitherto reported for monovalent ions. In the case of monovalent cations of K^+ and Na^+, an initial rise in the zeta potential is observed and then a gradual decrease. In the silver nitrate–silver case there is the initial sharp decrease, then a rise which is followed by the usual gradual decrease. This was at first attributed to experimental error, but check runs gave the same results.

In order to explain this unusual result it is necessary to consider the factors affecting the potential at the interface. If the diffuse double layer is considered as a plane condenser with the planes representing the average positions of the two layers, i.e., the electrogravitational planes, then the potential across these planes depends upon the distance between them and upon the charge density.

If the charge density is constant, then the difference in potential is directly proportional to the distance across the double layer, whereas, if the distance is kept constant, the potential is proportional to the charge density of the layers. This assumes that the dielectric constant does not change. However it may be considered as a constant factor, and as such will not affect the conclusions.

The distance across the double layer varies with the concentration of ions in the solution, the thickness being greatest in pure water and dilute solution. The first addition of electrolyte causes the greatest decrease in the distance, with successive additions causing less and less change. The potential should thus decrease sharply at first with a further fall occurring on addition of electrolyte. On the other hand, the addition of electrolyte will affect the charge on the double layer. If adsorption into the interface tends to increase the net charge of the double layer, i.e., by preferential adsorption of negative ions on a negatively charged fixed layer, then the potential will increase. If positive ions are adsorbed into the negative layer then the potential must decrease, for the charge is lowered.

The resultant change in potential must therefore depend on the relative magnitude of these three factors: (1) change in thickness of the double

layer, (2) adsorption of anions, and (3) adsorption of cations. Changes in these three factors have been used to account successfully for the changes which occur when solutions of such salts as potassium chloride, sodium chloride, etc., are streamed through glass capillaries. In the case of the silver–silver ion system, changes in the relative magnitude of the three factors give rise to a different type of potential curve. It is probable that the heavy metal ion is adsorbed to a much greater degree than was the case with the alkali cations. This effect, together with any drop in potential due to the shrinkage in the double layer, probably more than balances the effect of anion adsorption. On increased concentration the effect of shrinkage in the double layer becomes less significant, and we have the usual rise in potential due to preferential anion adsorption. As the double layer becomes more nearly saturated with ions, we obtain the final gradual fall in potential due to the decrease in double layer thickness.

The electrokinetic potentials of the silver–silver ion system differ from those of the nickel–nickel ion system. However they both exhibit changes in the ζ-potential which are unpredictable on the basis of consideration of the ϵ-potential theory. The Nernst potentials over this same concentration range vary in a perfectly regular manner. The variations in the electrokinetic potential depend upon the nature of the substances concerned and the concentration of the electrolyte. The Nernst potential, ϵ, depends upon one variable factor, the osmotic pressure of those ions which the metal supplies and a factor which is constant for each metal, the electrolytic solution pressure.

SUMMARY

A streaming potential method for the determination of the electrokinetic potentials of metals in contact with their ions has been developed, and measurements were made on the systems silver–silver ion and nickel–nickel ion, as well as on pure silica gel.

Metallized silica gels were used in the investigation. They were prepared by the new process of adsorbing complex ions of ammonia on the silica gel and later reducing to the metallic state.

A vacuum tube potentiometer and a vacuum tube conductivity bridge have been adapted to this type of work with excellent results.

Fundamental differences between the electrokinetic potentials and the Nernst potentials were found for the systems studied.

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THE AUTOXIDATION OF STANNOUS CHLORIDE. IV

The Effect of Some Non-aqueous Solvents[1]

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Previous work by the authors (4) has shown that the autoxidation of stannous chloride is a thermal and photochemical chain reaction, showing peroxide formation, induced oxidation of other molecular species present in the solution, and great sensitivity to positive and negative catalysts. The complex $HSnCl_3$ or H_2SnCl_4 was described as playing an important rôle in the oxidation of the stannous chloride.

Because of the interference of hydrolysis in the study of the reaction in aqueous solution, it was desired to determine the effect of acid concentration in some organic solvent. After many preliminary experiments, some of which are reported in paper II of this series (4), benzyl alcohol was finally selected as a suitable solvent.

AUTOXIDATION OF STANNOUS CHLORIDE IN BENZYL ALCOHOL

Benzyl alcohol was purified by vacuum distillation. The product boiled at 98–99°C. (uncorrected) at 17 mm. pressure, a value consistent with those recorded in the literature. Five different batches were prepared and found to give reproducible results. Dry hydrogen chloride was passed into the alcohol, and the solution was used immediately in order to prevent any invalidation of the results by the formation of benzyl chloride through esterification.

The autoxidation in benzyl alcohol was characterized by a short period of rapid absorption of oxygen, followed by a period of slow oxygen consumption, progressing toward complete oxidation. The initial period lasted from 5 to 8 minutes, and in order to express all data on a comparable basis, an arbitrary period of 10 minutes was taken, and the data expressed as the number of milliatoms of oxygen consumed in that time. This value, plotted against the normality of the hydrochloric acid, gives a straight line nearly to the point where the hydrochloric acid is equivalent to the stannous chloride, and then approaches a constant value. This effect was

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studied at two concentrations of stannous chloride, and the data are given in table 1 and figure 1. The effect of varying the concentration of the stannous chloride at a constant hydrochloric acid concentration was also studied at one acid concentration. These data are presented in table 2 and figure 2.

In both studies it will be noticed that the amount of oxygen consumed in the 10-minute period approaches a constant value as the variable concentration increases. The data for the variable stannous chloride concentration show this in the more pronounced way, since complete oxidation was not approached in the 10-minute absorption period in these runs.

TABLE 1

Effect of concentration of hydrochloric acid on the autoxidation of stannous chloride in benzyl alcohol

(A) STANNOUS CHLORIDE CONCENTRATION = 1.019 MILLIMOLES IN 25 CC		(B) STANNOUS CHLORIDE CONCENTRATION = 2.038 MILLIMOLES IN 25 CC.	
Concentration of hydrochloric acid	Oxygen used in 10 minutes	Concentration of hydrochloric acid	Oxygen used in 10 minutes
N	*milliatoms*	*N*	*milliatoms*
None	0.063	0 037	0.596
0.016	0.235	0.074	1.11
0.020	0.296	0.114	1.64
0.034	0.463	0.127	1.86
0.041	0.590	0.159	2.09
0.049	0.700	0.189	2.21
0.059	0.713	0.236	2.32
0.063	0.787	0 263	2.37
0.071	0.924	0.329	2.40
0.082	1.02		
0.095	1.13		
0.101	1.20		
0.221	1.18		
0.226	1.20		
0.233	1.23		
0.368	1.17		

It was found that induced oxidation of the benzyl alcohol occurs. At a stannous chloride concentration of 1.019 millimoles in 25 cc. of benzyl alcohol, and hydrochloric acid concentration varying from 0.10 *N* to 0.35 *N*, 1.21 milliatoms of oxygen were used, on the average. Since one milliatom of oxygen is equivalent to one millimole of stannous chloride, this was an excess of 18.6 per cent. Two runs with twice the amount of stannous chloride and an acid concentration of 0.25 *N* to 0.35 *N* gave practically the same value, 20.9 per cent.

The fact that the curves of figures 1 and 2 approach constant values,

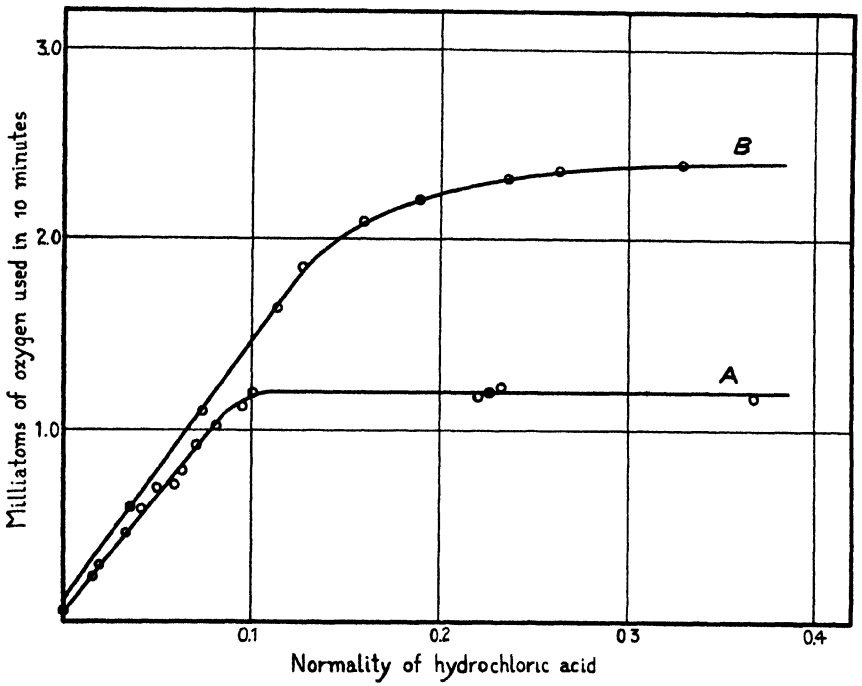

FIG. 1. THE EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID ON THE AUTOXIDATION OF STANNOUS CHLORIDE IN BENZYL ALCOHOL

A, stannous chloride concentration = 1.019 millimoles in 25 cc.; B, stannous chloride concentration = 2.038 millimoles in 25 cc.

TABLE 2

Effect of concentration of the stannous chloride on its autoxidation in benzyl alcohol

Hydrochloric acid concentration = 0.078 *N*

STANNOUS CHLORIDE CONCENTRATION	OXYGEN USED IN 10 MINUTES
millimoles in 25 cc.	*Milliatoms*
0	0
0.509	0.589
1.019	0.960*
1.528	1.18
2.038	1.18*
3.057	1.28
4.076	1.28

* Interpolated from figure 1.

shows again the presence of the equilibrium between stannous chloride and hydrochloric acid, and shows that these complexes are the principal forms

in which the stannous chloride is oxidized in benzyl alcohol. As the concentration of *either* of the constituents of the complex is increased, holding the other constant, the concentration of the complex, and thus the rate of oxidation, increases toward a constant value.

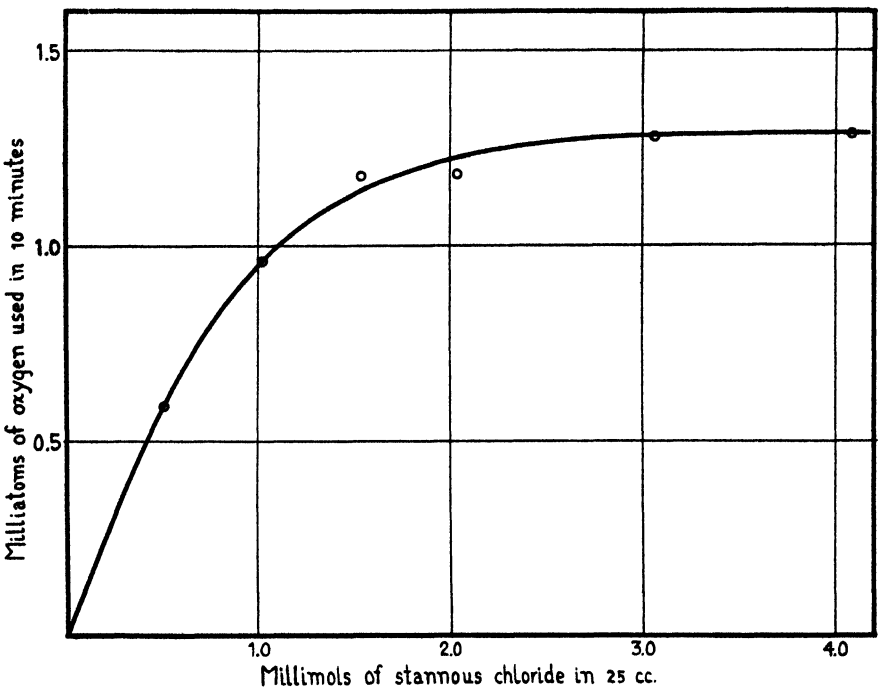

FIG. 2. THE EFFECT OF CONCENTRATION OF STANNOUS CHLORIDE ON ITS AUTOXIDATION IN BENZYL ALCOHOL

Hydrochloric acid concentration = 0.078 *N*

AUTOXIDATION OF STANNOUS CHLORIDE IN DIOXAN

A large amount of time was spent on the autoxidation of stannous chloride in dioxan (1,4-dioxane), since this solvent was expected to be very resistant to oxidation or reduction.

The dioxan was purified by refluxing for 7 to 12 hours with one-tenth its volume of 1 *N* hydrochloric acid to hydrolyze the acetal of ethylene glycol, which is always found as an impurity. Oxygen was passed through the ether during the hydrolysis to oxidize the aldehyde produced. The product was dried with solid potassium hydroxide, fractionated to remove low boiling material and the ethylene glycol, and finally was refluxed over molten sodium until no further reaction occurred, and the globules of sodium appeared bright (12 to 36 hours). The pure dioxan was then dis-

tilled from the sodium (boiling point, 99.7–99.9°C., uncorrected, at 740 mm.; freezing point, 11.80° ± 0.01°C.). This product is apparently of a higher degree of purity than that previously reported in the literature (1, 6).

Stannous chloride was found to form a molecular compound with dioxan in the ratio 1:1. The salt was recrystallized from dioxan of high purity, and the product analyzed. The percentages of chlorine and tin were found to be 25.40 and 43.12, as compared with 25.54 and 42.75 calculated for a 1:1 ratio of stannous chloride to dioxan.

This recrystallized molecular compound was used to determine the extent of complex formation between stannous chloride and hydrochloric acid in dioxan solution. This was determined by the method of freezing point lowering, for which the constant in dioxan is 5.0 (5). The freezing point lowering of solutions of stannous chloride and of hydrochloric acid in dioxan were determined, equal volumes of the two solutions mixed, and the freezing point lowering again determined.

TABLE 3

Complex formation between stannous chloride and hydrochloric acid in dioxan

STANNOUS CHLORIDE CONCENTRATION	HYDROCHLORIC ACID CONCENTRATION	FREEZING POINT LOWERING			
(Before mixing)		Obsd	Calcd (No complex)	Calcd ($HSnCl_3$)	Calcd (H_2SnCl_4)
M	*M*				
0.0315	0 1828	0 491°	0 536°	0 457°	0 378°
0.0315	0 3656	0 901	0 993	0 914	0 835

Complex formation is definitely shown in the data of table 3, which gives the experimental lowering compared with the theoretical lowering calculated (a) with no complex formation, (b) with all the stannous chloride present as $HSnCl_3$, and (c) with all the stannous chloride present as H_2SnCl_4.

High accuracy is not claimed for these results because of the extreme difficulty of preventing oxidation of the stannous chloride in acid concentrations as high as these. These determinations were made under nitrogen, and the solutions kept under nitrogen during as much of the handling as was possible, but a filtration was necessary, and a small amount of oxidation is very probable.

The autoxidation of stannous chloride in dioxan was found to resemble the oxidation in benzyl alcohol. There is a period of rapid absorption followed by a slow period in some runs. The oxidation is faster than in benzyl alcohol however, the initial rapid period being complete in 1½ minutes. In the purest samples, freshly distilled, the subsequent slow absorp-

tion was not present, but these samples of dioxan developed the slow absorption period after standing for several days, even under pure nitrogen. This effect is not due to water, since known amounts of water added to runs in freshly distilled dioxan do not produce the slow absorption period. Water does, however, increase the amount taken up in 1½ minutes of rapid absorption.

If oxygen is bubbled through an old sample of dioxan which shows the subsequent absorption period, just before its use in an autoxidation run, the subsequent absorption period is destroyed, and the amount of oxygen consumed in the initial period greatly reduced.

The results of the autoxidation could not be reproduced very well from one preparation of dioxan to the next, so that the results concerning the effect of hydrochloric acid concentration have no quantitative value, but about twenty-five runs in freshly distilled dioxan, out of more than a hundred, show a qualitative trend similar to that found with benzyl alcohol, that is, some oxygen is taken up even with no hydrochloric acid present; the amount of oxygen used up increases with the acid concentration, and approaches a constant value at high acid concentrations. Induced oxidation was also found, 1.01 millimoles of stannous chloride consuming 1.52 (average of ten runs) milliatoms of oxygen, an excess of 50.0 per cent.

Water added to the stannous chloride–hydrochloric acid–dioxan system was found to increase the amount of oxygen absorbed during the first 1½ minutes of the run. The amount of this increase was variable but ranged from 25 to 75 per cent for an addition of 0.10–0.30 g. of water.

Some preliminary experiments were also made in the following solvents: diamyl ether, dibenzyl ether, β,β'-dichlorodiethyl ether, nitrobenzene, diphenyl ether, and diethyl malonic ester. These all proved to be unsatisfactory from the standpoint of solubility, or reaction.

THE ACTION OF POSITIVE AND NEGATIVE CATALYSTS IN NON-AQUEOUS SOLVENTS

In order to correlate the reaction in organic solvents with the reaction in water, a few experiments were made with some positive and negative catalysts. Picric acid has been found to be a good inhibitor in aqueous solution, and it proved to be one in non-aqueous solvents as well. It was used, qualitatively, to inhibit the reaction in the following solvents: benzyl alcohol, β, β'-dichlorodiethyl ether, and glacial acetic acid. Its inhibitory power can best be shown by the acetic acid experiments. In this solvent one millimole of stannous chloride is oxidized in 2 minutes, whereas with 0.02 g. of picric acid added, less than 0.005 milliatom of oxygen is taken up in 20 minutes. *m*-Dinitrobenzene, *p*-aminophenol, and *p*-nitrotoluene were also found to be good inhibitors in acetic acid solution. All these

inhibitors seem to be more effective in acetic acid than they were in aqueous solution.

Thiourea, which is a strong accelerator in aqueous solution, also catalyzes in benzyl alcohol, and in β, β'-dichlorodiethyl ether, but 0.01 *M* accelerates the reaction only about 150 per cent as compared with about 2000 per cent in water. However, this may in part be due to the low solubility of thiourea in these solvents. Tetraethyllead was found to accelerate the reaction in benzyl alcohol as it did in water, but willow charcoal had the anomalous effect of showing no catalytic effect in benzyl alcohol.

DISCUSSION

In this paper further evidence has been presented to show that the chloro acid complexes are important in the mechanism of the autoxidation of stannous chloride. The approaching of a constant value for the rate of autoxidation with increasing concentration of *either* of the constituents of the complex indicates this, and it is further proven by the determination of complex formation in dioxan solution. The close analogy between the effect of hydrochloric acid on the reaction in water and organic solvents, and the identical action of inhibitors and accelerators show that the mechanism of the reaction is not affected appreciably by the solvents.

The summation of the work presented in this series of papers leads the authors to believe that the autoxidation of stannous chloride may be represented by the series of reactions designating the typical autoxidation, viz., if A and $\underline{A}$ represent autoxidant molecules (in this case $HSnCl_3$ or H_2SnCl_4) and * represents energy of vibrational activation (from thermal or photochemical sources), then

$$A + * \rightarrow A^* \tag{1}$$

$$A^* + O_2 \rightarrow AO_2^* \tag{2}$$

$$AO_2^* + \underline{A} \rightarrow A^* + \underline{A}O_2 \tag{3}$$

$$AO_2^* + I \rightarrow AO + IO^* \tag{4}$$

$$\underline{A}O_2 + A \rightarrow 2AO \tag{5}$$

The symbol $\underline{A}$ is used to show the transfer of two atoms of oxygen instead of an energy transfer. This mechanism was proposed by Bodenstein (3), and amplified by Bäckström and Beatty (2). I represents the inhibitor molecule, and the IO* molecule has a lower specific reaction rate with $\underline{A}$ than has the activated peroxide AO_2^*. Thus the widely differing powers of various inhibitors in a reaction are due to their differing abilities to react with $\underline{A}$ and perpetuate the reaction chain. This also accounts for the ability of one substance to be an inhibitor for one reaction and an accelerator for another, since the effect the substance has will depend on the reac-

tive ability of its oxide (or peroxide) *relative* to that of the autoxidant. In this general scheme, the reaction chain is reaction 1 followed by an alternation between reactions 2 and 3, while reaction 4 is the chain-breaking mechanism. Reaction 5 occurs subsequent to the chain, and may, under the proper conditions, be slowed sufficiently to permit the detection, and even the isolation, of the peroxide, as has been reported by many investigators in widely differing reactions.

SUMMARY

1. Very pure dioxan (f.p. = 11.80 ±0.01°C.) has been prepared, and complex formation shown between stannous chloride and hydrochloric acid by means of freezing point lowering in this solvent.

2. A molecular compound of one mole of stannous chloride with one mole of dioxan has been identified by analysis.

3. The rate of autoxidation of stannous chloride in dioxan and in benzyl alcohol has been studied. It was found to increase nearly linearly with the acid concentration up to a point where the acid concentration is close to that of the stannous chloride, and then to approach a constant value.

4. The postulation of the chloro acid complex as the form in which the stannous chloride is oxidized was confirmed by the above experiments, and by those in which the rate also approached a constant value with increasing stannous chloride concentration, at a constant acid concentration.

5. Induced oxidation of dioxan and benzyl alcohol was demonstrated during the autoxidation of stannous chloride in those solvents.

6. Several positive and negative catalysts were shown to have qualitatively the same effect in non-aqueous solvents as they have in aqueous solution.

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A STUDY OF THE INFLUENCE OF AN ELECTRIC FIELD ON THE POTENTIAL AT A METAL-SOLUTION INTERFACE

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Numerous studies have been made on the electrical potential difference between a metal and an aqueous solution which does not contain a salt of the metal but contains other electrolytes and dissolved gases. The so-called oxygen electrode in particular has received much attention (5, 6, 9, 10, 16, 21, 23, 25). The influence of the movement of the electrolyte on such a potential difference has also been investigated (1, 11, 19, 20, 22, 26).

These electrical potentials are of considerable significance. Many are the systems that present the contact of a metal with an aqueous solution containing few if any of the metal ions. Colloidal metals such as platinum, silver, and gold reveal systems which owe their stability and cataphoretic behavior to the potential between the colloidal metallic particle and the dispersion medium. It is well-known, too, that the electrolyte present markedly influences the potential of such a metal-liquid interface.

In treating the electrical potential across this type of metal-liquid interface, investigators have considered two potentials. The first is the Nernst potential obtained by the usual potentiometric determination of the potential difference by the use of a standard half-cell. The second is the electrokinetic or "zeta" potential between the liquid adhering to the solid wall and the bulk of the mobile liquid. This is always estimated by a hypothetical consideration of the data from experiments on cataphoresis, electroösmosis, or streaming potentials.

If the accepted theory of electrokinetic phenomena is correct there should be some relation between changes in the zeta potential and the Nernst potential. All experimental evidence points to the interface as the region in which these changes which affect the electrokinetic potential occur, and certainly the Nernst potential extends across this interface.

The effect of mechanical and electrical forces acting on the potential at the metal-electrolyte interface should afford information that can be used in determining the nature of this potential. The results might also be applicable in the development of a satisfactory theory of electrokinetic phenomena and the zeta potential. The very imperfect status of our

knowledge of this topic has been adequately summarized by McBain (12, 13).

The work presented in this paper is an attempt to determine the effect of an electric field on the potential at the interface metal–electrolyte. The way in which this was accomplished is indicated by the following considerations.

The potential of a cell under ordinary circumstances may be considered as made up of two parts: first, of the potential of metal, electrolyte (dissolved gas) (E_m); and second, of the potential of electrolyte (dissolved gas), half-cell (= constant). The potential of the cell is

$$E = E_m + \text{Constant} \tag{1}$$

If there exists in the electrolyte an impressed potential gradient, the potential of the cell will contain an additional term Fx, where F is the field strength in volts per centimeter, and x is the distance in centimeters between the electrode and the tip of the half-cell bridge, measured parallel to the direction of the field. The potential of this cell is

$$E' = E'_m + Fx + \text{Constant} \tag{2}$$

Then

$$E - E' = E_m - E'_m - Fx \tag{3}$$

By adjusting the position of the electrode and bridge it is possible to make $x = 0$, whence

$$E - E' = E_m - E'_m$$

EXPERIMENTAL

The experimental set-up consisted of a small rectangular electrolysis vessel fitted at each end with electrodes, which, when differently charged, produced a potential gradient through the solution. The experimental electrode and half-cell bridge were placed in this field in a position such that $x = 0$ (equation 3). The set-up is shown in figure 1.

The electrolysis vessel (M) was a rectangular glass trough, 7.5 × 2.5 × 2.5 cm., which was fitted at each end with a sheet of platinum (F) which served as a field electrode. The glass–glass and glass–platinum contacts were sealed with picein wax in some experiments and with de Khotinsky cement in others. The electrolysis vessel was fixed with appropriate insulation in a small wooden box which was lined with metal foil electrically grounded.

The experimental electrodes (E) were very small, which reduced conduction through the metal. It was thought that the factors involved might better be differentiated by the use of differently shaped electrodes. Since a flat surface might give different results than a curved surface, two types

of electrodes were used. Type A electrodes were made by covering the tip of the wire with a glass bead and then sealing the wire into a small thin glass tube, leaving a 1-mm. length of wire uncovered. Type B electrodes were made by sealing the wire in a small thin glass rod and then, by grinding and polishing, the metal and glass were smoothed. This gave a very small electrode surface which was exactly flush with the glass surrounding it.

Electrodes were made of platinum and of gold wire, each as pure as was possible to obtain. These metals were used because there are experimental data in the literature on the cataphoresis of gold and platinum sols. The gold wire was 0.0193 cm. in diameter. Two sizes of platinum wire were used,—0.0315 cm. in diameter and 0.0193 cm. in diameter.

The other half of the cell measured was a normal calomel electrode (C), connected through a bridge (L) which contained 0.1 *M* potassium chloride

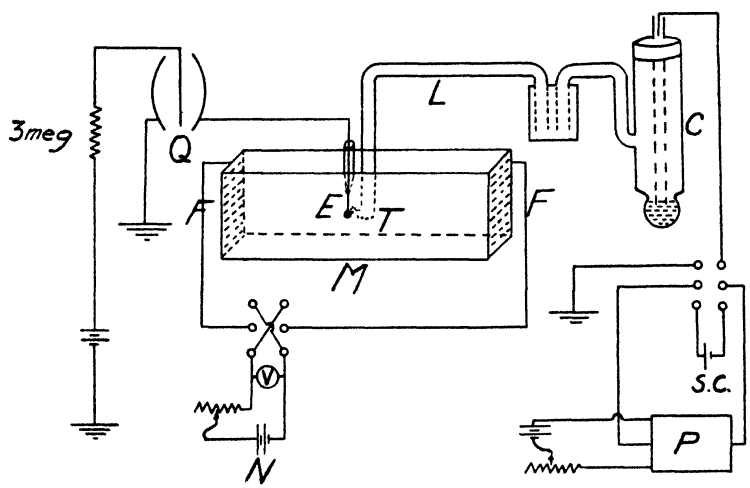

FIG. 1. ELECTRICAL CIRCUITS (diagrammatic)

in an agar gel. The end of the bridge (T) in the electrolysis vessel was drawn out to a very fine tip which turned at right angles to the bridge tube. The size of the opening of the bridge tip was found to make no difference when it was of the same order of magnitude as that of the electrode. This was carefully checked by the use of different bridge tips of widely varying diameter.

The bridge was held in place by a clamp which was attached to a long lever arm. One end of the lever arm was fastened to a rigid upright rod about which the lever could turn; the other end was moved by means of a screw which could be set to 0.003 mm. The screw had a mechanical advantage of 4 over the tip of the bridge, which facilitated accurate setting of the bridge tip with respect to the experimental electrode.

The potential for the applied field was obtained from a large size "B" battery (N), which was connected to the field electrodes at the ends of the electrolysis vessel through a commutator which reversed the field every 1.8 seconds. The potential of the experimental electrode was affected in the same way by a field which was reversed every 50 seconds, but the shorter period proved most convenient. The field could not be reversed too rapidly, because the electrometer needle would not follow accurately the changes in the measured potential when $x \neq 0$. This change in the direction of the field reduced polarization at the field electrodes, which increased the agreement between the calculated and actual values of the field strength. Both "B" battery and commutator were supported by sulfur blocks.

The potential of the cell:

metal, electrolyte (dissolved gas), 0.1 *M* KCl, 1 *M* KCl, HgCl, Hg

was measured by means of a Leeds and Northrup potentiometer and a quadrant electrometer of the Compton type (Q) as shown in figure 1. It is necessary that the experimental electrode be connected to the electrometer, because otherwise circuit leakage may cause a current through the electrode.

The sensitivity of the electrometer varied from day to day, but was always in the neighborhood of 700 cm. per volt on a scale 1 meter distant, but the scale actually used was placed at a distance of 3.4 m. and was illuminated.

The first step in setting up the apparatus was to clamp the electrolytic vessel firmly in place. Then the leads from the commutator were connected to the field electrodes, and the glass rod holding the electrode was fixed in such a manner that the experimental electrode was held in the center of the electrolysis vessel.

The electrodes were placed so that the smooth metal surface of the type B electrodes was parallel to the direction of the field and the axis of the cylinder of the type A electrodes was perpendicular to the direction of the field. Great care was necessary in the adjustment of the cylindrical electrodes, because if the angle was much less than 90° the electrode potential became very erratic. The flat electrodes were not so sensitive, but gave best results when carefully adjusted.

When the experimental electrode was in place, the bridge was set so that the tip was within 2 mm. of the electrode. The smaller the distance between them, the easier it was to adjust the bridge to the correct position.

After filling the electrolysis vessel with the solution, the potential of the electrode was read at intervals until it had become fairly constant. In some cases this took a long time and in others only an hour or two. When the potential had become nearly steady the key to the electrometer was

clamped down so that the potential could be followed continuously. Next the commutator was started and the field turned on. The measured potential changed as the field was reversed, owing to the factor Fx (see equation 2). This could readily be observed as the electrometer needle swung back and forth, but when the bridge had been set carefully this factor was only about 20 millivolts. Next the position of the bridge was adjusted so that the electrometer needle became stationary, and the

TABLE 1

Change in millivolts of the potential of gold electrodes caused by fields of value F volts per centimeter ($E_m - E_m'$)

ELECTROLYTE	MOLARITY	ELECTRODE DIAMETER 0 0193 CM.		
		Type A		Type B
		F = 2 2	F = 3.1	F = 3 1
H_3BO_3	10^{-6}	1		0
	10^{-5}	0		0
	10^{-4}	0		0
	10^{-3}	0		0
	10^{-2}	0		0
KH_2PO_4	10^{-6}		0	0
	10^{-5}		0	0
	10^{-4}		0	0
	10^{-3}		0	0
	10^{-2}		−1	0
Na_2HPO_4	10^{-6}		0	0
	10^{-5}		0	0
	10^{-4}		0	0
	10^{-3}		0	0
	10^{-2}		−1	1
$Al_2(SO_4)_3$*	10^{-6}		0	0
	10^{-5}		0	0
	10^{-4}		0	0
	10^{-3}		−1	0
	10^{-2}		−1	0

* Contained hydrochloric acid at a concentration one-tenth that of the aluminum sulfate.

potential of the cell was measured. When the needle was stationary, ($x = 0$, $\therefore Fx = 0$) $E_0' = E_m' +$ Constant. The field was turned off and the potential of the electrode measured. The difference between these two potentials is the value $E_m - E_m'$.

It was found that the length of time the field was on in one direction did not necessarily need to be the same as the length of time in the other direction. Various ratios of these two periods were tried and the results were the same in all except the extremes, where the ratio was 1:5.

It was thought that perhaps the position of the electrometer needle with respect to the quadrants might have an influence on the measurement of the potential. To check this the measurement was carried out in three different ways. First, the potentiometer was set so that when the needle was brought to rest by adjusting the position of the bridge, it was turned to

TABLE 2

Change in millivolts of the potential of platinum electrodes caused by fields of value F volts per centimeter ($E_m - E_m'$)

ELECTROLYTE	MOLARITY	ELECTRODE DIAMETER 0 0315 CM.				ELECTRODE DIAMETER 0 0193 CM.	
		Type A		Type B		Type A	Type B
		$F = 2.5$	$F = 2.1$	$F = 3.1$	$F = 6.2$	$F = 3.1$	$F = 3.1$
H_3BO_3	10^{-6}	1		0	0	0	0
	10^{-5}	0		0	1	0	1
					3		
	10^{-4}	2		0	1	0	0
	10^{-3}	1		0	2	2	0
	10^{-2}	0		0	1	2	0
KH_2PO_4	10^{-6}		0	0	3	0	0
	10^{-5}		0	0	1	0	0
	10^{-4}		0	0	2	0	0
	10^{-3}		0	0	0	0	0
					1		
	10^{-2}		0	0	0	0	0
					−1		
Na_2HPO_4	10^{-6}		0	0	2	1.5	0
	10^{-5}		0	2	3	−1	0
	10^{-4}		0	1	3	0	0
	10^{-3}		0	1	3	2	0
	10^{-2}		0	1	1.5	0	0
$Al_2(SO_4)_3$*	10^{-6}		0	1	2	0	0
	10^{-5}		0	1	3	0	0
	10^{-4}		2	0	1	0	0
	10^{-3}		0	2	2	0	0
	10^{-2}		0	†	†	0	0

* Contained hydrochloric acid at a concentration one-tenth that of the aluminum sulfate.

† Potential too unstable to give results.

the left of the zero point. This was repeated with the potentiometer set first so that the needle was at the zero point and then to the right of the zero point. The potential calculated from the deflection, the sensitivity, and the potentiometer reading was the same in each case, which showed that the position of the needle with respect to the quadrants was not a source of

error in the measurements. The quickest method of measurement was to bring the needle to the zero position by changing the potentiometer setting.

No attempt was made to have pure gases over the solution since it is our experience (24) that air or oxygen gives a very sensitive potential with electrodes of this type.

The materials used were well purified and the solutions were made up with a good grade of conductivity water which contained dissolved air. The experiments were carried out in a room which was held at 20 ± 1°C.

The procedure described above was carried out for solutions of several compounds. The range of concentrations employed was from 10^{-6} to 10^{-2} molar. The compounds used were those which previous work (24) had indicated would be most likely to produce the most favorable conditions for a change in potential of the electrode. The concentrations studied were chosen after a consideration of the effects of electrolytes on cataphoresis and streaming potentials. More concentrated solutions could not be used because of the increased conductance of the electrolysis cell.

Tables 1 and 2 give the values of $E_m - E_m'$ for the several electrodes in the different solutions.

For field strengths greater than those reported above, the change in potential was entirely different in character. The potential became so unsteady and unreproducible that it was evident that some new factor had been brought in. Furthermore, recovery by the electrode of its original potential was very slow. A second difficulty of the stronger fields was the fact that the bridge could not be set accurately enough to eliminate completely the oscillations of the electrometer needle.

DISCUSSION

The data presented above show that the potential of gold or platinum against a solution is only slightly affected by an electric field of moderate strength. The changes in potential which do occur may be due to any one of several factors.

a. Conduction through the electrode

If an appreciable current flowed through the metal there might be some hydrogen or oxygen liberated which would change the potential. This explanation of the change does not seem probable when we consider that the changes occur as frequently in the two most dilute solutions as in the two most concentrated solutions.

The instability and change of the potential of electrodes of type A in strong fields was attributed to conduction, because any change in conditions which would increase conduction through the electrode always increased the instability of the potential. The rate at which the electrode recovered the original potential was very slow, which was probably due to the slow change in amount of gas at the surface of the electrode.

These results throw some doubt on the deductions of Coehn and Schafmeister (2) and of Theissen and Heumann (27). These workers used a small metal wire suspended in electrolytes through which the field drop was 110 and 46 volts per centimeter, respectively. They measured the deflection of the wire caused by the field, then determined the potential of the metal in the same solution when there was no potential gradient through it. Our results indicate that the potentials measured by these workers were quite different from the potentials of the wires when the field was on. It is impossible to estimate what error appeared in their work, because the fields they used were from fourteen to thirty-five times as strong as those used in our experiments.

b. Surface conduction

McBain and his coworkers (14, 15) have shown that the electrical conductivity at a glass–solution interface is greater than in the bulk of the solution, and this same phenomenon may occur at a metal–solution interface. The movement of ions longitudinally through the diffuse double layer would somewhat change the distribution in the double layer and would, if the distribution were sufficiently disturbed, cause a change in the potential.

It was found that the addition of a small amount of a substance which is known to be highly absorbed at the metal–liquid interface, such as tannic acid or gelatin, would reduce the change in potential of the small cylindrical platinum electrodes. A thin coating of collodion would accomplish the same result. This indicates that the change occurs at the interface.

Whatever may be the true cause of the observed changes of potential brought about by the electric field, the results have a very significant value to the theory of electrokinetic phenomena.

The experimental results reported show that the potentials of the smallest electrodes are affected least by the electric field. Going further one may say that the potential of an electrode the size of a colloidal particle would not be affected at all. That small platinum or gold wires in an electric field behave similarly to a platinum or gold sol has been shown by Kleeman and Fredricksen (7).

The results further show that a greater change is observed when the field strength is increased. The field strengths used in the ordinary measurement of cataphoretic velocities of gold and of platinum sols (8, 18) are less than those used in these experiments. Therefore we can conclude that in cataphoresis experiments of gold and platinum sols, the Nernst potential of the gold or platinum against the solution is unchanged by the field.

If we consider one side of the "double layer" as diffuse, after Gouy (4), and develop the idea of the relation between the Nernst potential and the zeta potential as was done by Smoluchowski (3), we find that the Nernst

potential contains the zeta potential. It is evident that since the Nernst potential of gold or platinum colloidal particles is unaffected by the applied electrical field, we are certain that the zeta potential also is unchanged by the same conditions.

The potential across the double layer depends upon the charge per unit area and also upon the charge distribution in the outer or diffuse layer. One would not expect an applied field to affect the charge per unit area. Furthermore, it is almost beyond the bounds of possibility that, if the charge per unit area were affected, the outer or diffuse layer would be affected an exactly equal amount in the opposite direction, which would be necessary in order for the potential to remain the same. Therefore, since the zeta potential of a colloidal particle remains constant, we must conclude that the charge distribution, or its physical symmetry, in the diffuse layer is unaffected by an electric field of the strength used in cataphoresis experiments.

This assumption is common to both the Helmholtz-Lamb and Debye-Hückel theories of cataphoresis (17). Actual experimental tests of the other assumptions will be of great value in testing these theories, and in the ultimate explanation of the mechanism of cataphoresis. A more extensive knowledge of the interface is also necessary for a more complete explanation of the potential of the oxygen electrode.

SUMMARY

The effect of an electric field of moderate strength on the potentials of gold and platinum against several solutions has been determined.

The results prove the validity of one fundamental assumption in the treatment of cataphoresis, namely, that the charge distribution in the double layer is unaffected by an applied field of the strength used in cataphoresis experiments.

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HALIDE–IODINE EQUILIBRIA IN NEUTRAL SALT SOLVENTS[1]

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I. INTRODUCTION

Interest in the triiodide equilibrium

$$I_3^- \rightleftharpoons I_2 + I^- \tag{1a}$$

was renewed with the appearance of a paper by Brönsted and Pedersen (1922) (1). These authors determined the solubility of iodine in an aqueous solution of 1.65 molar potassium chloride with sufficient hydrochloric acid to produce an acidity of pH 5, thereby preventing hydrolysis[2] (2). By measuring the increase in the solubility of iodine produced by the addition of relatively small amounts of potassium iodide at 15° and 18.5°C., they gave an extrapolated value for the mass action function,

$$L = \frac{c_{I_2} \times c_{I^-}}{c_{I_3^-}}$$

namely, 0.00611 for 25°C. In calculating L they considered this increase in the solubility of iodine as triiodide and the concentration of free iodine equal to the solubility of iodine in the potassium chloride solvent.

Their purpose in employing 1.65 molar potassium chloride as solvent was to minimize the changes in ionic environment (3) produced by varying the concentration of added potassium iodide.

Carter and Hoskins (1928) (4) pointed out that Brönsted and Pedersen failed to recognize the possibility of a salting-out effect of the chloride ion on the neutral molecule, iodine, and the formation of a chloride–iodine complex:

$$ClI_2^- \rightleftharpoons I_2 + Cl^- \tag{1b}$$

[1] This paper was constructed from a dissertation submitted by M. Helene Lewinsohn in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1933.

[2] The reactions are:

$$I_2 + H_2O \rightleftharpoons H^+ + I^- + HIO$$
$$3I_2 + 3H_2O \rightleftharpoons 6H^+ + 5I^- + IO_3^-$$

Iodine on dissolving in water may be interpreted as undergoing internal oxidation and reduction.

Carter and Hoskins also asserted that "when suitable corrections are made for the disturbing effect of polyhalide formation, it is found that the resulting value of K is approximately the same as when the solvent is water." However, they submitted no experimental proof for this statement. This important conclusion was also tacitly assumed by Kiss and Urmanczy (1931) (5). It may be interpreted as a reiteration of part of the well-established principle enunciated by Brönsted (6); namely, "that the simple gas laws hold good for ions or salts when other salt solutions are employed as solvents, the concentration being large in comparison with the dissolved ion or ions," i.e., in a constant ionic environment. This principle involves two fundamental ideas; namely, that the concentration of the salt serving as solvent is large in comparison with the dissolved ion and that the solvent salt gives no evidence of interacting chemically with the dissolved molecule or ion.

These two conflicting opinions and the fact that the triiodide constant frequently enters into the interpretation of the equilibria involving iodine occasioned this investigation, the purpose being to determine this constant, $K_{c_{I_3^-}}$, in solvents of constant thermodynamic environment in a manner which would be free from the objections raised by Carter and Hoskins.

In order to test the applicability of Brönsted's principle to the aforementioned equilibria it was necessary to establish the following:

(1) The solubility of iodine in water at pH 5 with a greater precision than had been heretofore obtained.

(2) The values for the mass action functions for the three equilibria

$$ClI_2^- \rightleftharpoons I_2 + Cl^- \tag{1b}$$

$$BrI_2^- \rightleftharpoons I_2 + Br^- \tag{1c}$$

$$I_3^- \rightleftharpoons I_2 + I^- \tag{1a}$$

in high concentration (2 molar) of a salt, such as potassium nitrate, which gives no evidence of interacting chemically with iodine.

(3) The constancy of the mass action function for the triiodide equilibrium,

$$I_3^- \rightleftharpoons I_2 + I^- \tag{1a}$$

in a high concentration of potassium chloride, which salt, however, gives evidence of combining chemically with iodine.

In each of the above equilibria, the excess iodine dissolved in a halide salt solvent shall be designated as halide–iodine complex, and by measuring this increase in solubility the values for the mass action function will be calculated.

II. EXPERIMENTAL

The following are the source, preparation, and purification of chemicals required in the course of solubility measurements.

Potassium nitrate and potassium chloride were recrystallized twice from distilled water, dried in an oven at 120°C., ground in an agate mortar, and dried again at 120°C. for twenty-four hours. The salts were kept in a desiccator over calcium chloride until cool, then the samples were weighed.

Potassium bromide, Kahlbaum's "Zur Analyse," was dried in an oven at 120°C. and was kept in a desiccator over calcium chloride.

Potassium iodide, Mallinckrodt "Reagent Quality," was kept in a desiccator over phosphorus pentoxide. Samples gave no color with starch in neutral solution after twenty-four hours in the dark and no color with starch after acidification.

Iodine was resublimed once from a mixture of potassium iodide and iodine and twice without potassium iodide. The iodine was kept over calcium chloride in a desiccator, the cover of which had not been greased (7). Solutions of iodine containing 4 per cent potassium iodide (8) were used as primary standards.

Solutions of arsenious oxide, standardized against iodine solutions, were used as secondary standards. All titrations were made in bicarbonate buffers according to the directions of Washburn (8), using weight-burets (9).

The concentration of iodine necessary to produce a detectable color with the sterilized starch paste was of the order of 5×10^{-6} normal, and appropriate corrections were made.

Nitrogen, commercial, was purified by passing it through a solution of potassium pyrogallate (10), over heated copper gauze in a quartz tube, through dilute sulfuric acid, thence through a tube filled with soda lime. Finally, nitrogen was bubbled through the solvent solution so as to insure the same aqueous tension.

All salt solutions in which the solubility of iodine was to be determined were maintained at a pH of 5 to prevent hydrolysis of the iodine (see footnote 2) (2). This pH was adjusted by indicators.

All solubility measurements are reported as moles per liter of solution and were performed at 25 ±0.005°C.

Procedure in determining solubilities

The apparatus used is shown in figure 1, and is similar in principle to that used by Brönsted and Pedersen (1).

The solubility tube B was filled with a mixture of iodine and glass beads, and was plugged at the lower end with silica fiber and at the upper end with glass wool[3], since silica fiber proved to be too brittle to serve as a plug.

[3] This experimental work was considerably delayed by the inability to obtain reproducible values for the solubility of iodine. This difficulty was traced to the

Flasks D, E, and F contained iodine crystals to maintain a constant vapor pressure of iodine. Flasks E and F contained in addition to the iodine crystals about 50 cc. of the solvent to serve as an extra precaution to saturate the nitrogen entering at 5 and 7 with respect to iodine and water vapor. Nitrogen was passed through stopcocks 4, 5, and 6 for 3 hours and through the solution in flask A in the ratio of one hour for each 50 cc. of solution to displace oxygen.

To flush the contents of the solubility tube B and to insure complete removal of the previous solution of different concentration, one portion of

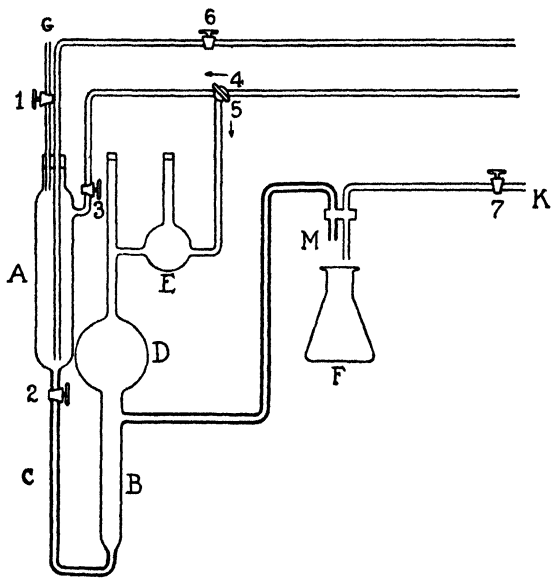

FIG. 1

25 cc. and two portions of 50 cc. each of solution were placed in flask A. The solution passed at the rate of 50 cc. of solution in 25 minutes, over the iodine into flask D, and remained there for 20 minutes. Pressure of nitrogen then forced the solution into flask F, gentle suction being applied at K. However, some of the solution remained in tube B, and was removed to

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alkaline reaction produced by the dissolving of the glass wool used as filter. Ten different samples of glass wool were tested as follows: 10 g. of glass wool were left in contact with 250 cc. of distilled water. After 4 hours these samples of glass wool yielded pH values ranging from 7.8 to 10.6, which did not change on standing. Alkali-free glass wool was essential to obtain concordant values for the solubility of iodine, for any other glass wool rendered the solutions basic and formed hypoiodites by the hydrolysis of iodine. The firm of Friedrich and Dimmock of Millville, New Jersey, spun especially some alkali-free glass wool which yielded an equilibrium pH of 6.8.

flask A by suction applied at G. This procedure was repeated four times to assure complete removal of the previous solution.

One hundred and fifty cubic centimeters of the solvent were placed in flask A, and the air was replaced by nitrogen. The solvent was passed through the iodine crystals into flask D, and thence back to flask A. A 150-cc. sample was taken so that each run could be separated into two parts, the second half passing through the solute at least four times. In each case there were at least two samples of 150 cc. each, thereby giving four weight-buretfuls and a minimum of ten titrations for the iodine concentration for each solubility measurement.

The sample in which the concentration of iodine was to be determined was transferred as follows: Flask F was removed. The saturated iodine solution flowed from the solubility tube B directly into a weight-buret, suspended under M, containing 5 cc. of a concentrated potassium iodide solution to prevent loss of iodine during transfer and subsequent titrations.

TABLE 1

Solubility of iodine

2 *M* KNO_3 + 0 0025 *M* KI		1.65 *M* KCl + 0 1 *M* KI	
TIMES SOLUTION OVER IODINE	SOLUBILITY VALUE $\times 10^6$	TIME SOLUTION IN CONTACT WITH IODINE	SOLUBILITY VALUE $\times 10^6$
4	2137 ±2	Overnight	4421 ±1 4
6	2138 ±2	2.5 days	4418 ±2 5
2	2139 ±1 6	Overnight	4420 ±2 2
5	2140 ±1.4	7 5 days	4425
	2138.5 (average)		4421 0 (average)

Kolthoff (11) states that in a solution less concentrated than 0.01 molar, the color appears somewhat too late in titrations of sodium thiosulfate with iodine, using starch as an indicator. This was found not to be true when arsenious oxide was used as the reductant. Solutions faintly colored blue with starch iodine were left for about seventeen hours and there was no perceptible color change. This indicates that there was no retardation in the appearance of the end point, and that the resultant solution had the correct pH according to Washburn (8). All titrations were made by daylight.

After six different determinations had been made, it was found necessary to refill the solubility tube B. This probably was due to the contamination of the iodine in tube B with traces of stopcock grease (7).

The proofs that solubility equilibrium was obtained are as follows: (1) A solution saturated with iodine at 30°C. was passed over the iodine at 25°C.; a solution saturated with iodine at 25°C. was passed over the iodine at 25°C. The solubility values in the two cases were within limits of

experimental error. By the former method the solubility of iodine in a 1.65 molar potassium chloride solvent was found to be $0.003534 \pm 4 \times 10^{-6}$; by the latter, $0.0035336 \pm 5 \times 10^{-7}$. (2) Less than 0.15 per cent change in the solubility value was found by passing the solution over the solid phase as many as six times, or by allowing the solution to remain in contact with iodine for a maximum time of seven days (see table 1).

III. PRESENTATION AND DISCUSSION OF EXPERIMENTAL DATA

Solubility of iodine in water

As a mean of six experiments the solubility of iodine in water at pH 5 was found to have been 0.001321 moles per liter of solution, thus substantiating the value of Carter (12) and of Bray (2), the latter to within 0.1

TABLE 2

Solubility of iodine in water

SOLUBILITY OF IODINE	pH VALUE	DATE	INVESTIGATOR
0.001337		1894	Jakowkin (13)
$0.001341 \pm 4 \times 10^{-6}$		1898	Noyes and Seidensticker (14)
0.001333		1908	Campbell and Hartley (15)
0.001320 calculated	Acid solution	1910	Bray (2)
0.001310		1920	Oliveri, Mandala, and Angencia (16)
0.001329	Conductivity water	1924	Pearce and Eversole (17)
$0.001321 \pm 2 \times 10^{-6}$	5	1925	Carter (12)
$0.001321 \pm 2 \times 10^{-6}$	5	1930	Present investigation
$0.001332 \pm 3 \times 10^{-6}$		1931	Kiss and Urmanczy (5)

per cent. Table 2 cites the values for this solubility appearing in the literature.

Theoretical

It is a well-known fact that the addition of a neutral salt to a system in equilibrium with the solid phase changes the solubility of the non-electrolyte, i.e., salting out the neutral molecule. The amount salted out depends upon the specific properties of the non-electrolyte, or neutral molecule, and the added salt,—the dielectric constant of the medium, the radius of the ion, and the distance of closest approach of ion to non-electrolyte. The total decrease in the concentration of the non-electrolyte or that salted out by a single ion has been recently calculated by Butler (18) and is equivalent to that calculated by Debye and McAulay (19), except for the fact that the latter equation requires the dielectric constant of the pure solvent and the former that of the solution. Experimental data have been examined from the point of view of the Debye-McAulay

equation by Randall and Failey (20) who conclude that, "there seems to be a qualitative agreement with the demands (of the equation) in most cases, but not a quantitative one." Unfortunately, at the present time, there is not sufficient independent data to make the equations of Butler or of Debye and McAulay feasible for this problem. Consequently, in this report the values for the salting-out constants are those given by Kiss and Urmanczy (5).

These authors[4] calculate the salting-out constant in the Setschenow equation (21),

$$\log s = \log s_0 - kC \tag{2}$$

where s_0 is the measured solubility of iodine in water at pH 5,
s is the calculated concentration of the iodine molecule,
C is the measured concentration of the solvent salt, and
k is the salting-out constant.

The average of these values for k is used as the salting-out constant and the concentration of free iodine is determined by means of the same equation. This direct method is used for salts like potassium nitrate, sodium sulfate, etc., which salts give no evidence of combining with iodine. Values for k for these salts using either acetylene or nitrous oxide or both as solutes are calculated. From these values the following average ratios are observed:

$$\frac{k_{C_2H_2}}{k_{I_2}} = 1.15 \quad \text{and} \quad \frac{k_{N_2O}}{k_{I_2}} = 1.25$$

Therefore, for salts like potassium chloride, magnesium chloride, potassium bromide, etc., which give evidence of combining chemically with iodine, the k for iodine has to be determined indirectly and the preceding approximations are used. At best, the values for k and s so calculated are subject to error.

The concentration of iodine, of chloride, bromide, and iodide, and of chloride–iodine, bromide–iodine, and triiodide ions and the mass action functions are calculated as follows. s_0, s, and C have the same significance as previously stated, and S is the measured (total) solubility of iodine as I_2, ClI_2^-, etc. Then for the assumed equilibria, namely,

$$ClI_2^- \rightleftharpoons I_2 + Cl^- \tag{1b}$$

$$BrI_2^- \rightleftharpoons I_2 + Br^- \tag{1c}$$

$$I_3^- \rightleftharpoons I_2 + I^- \tag{1a}$$

[4] Whenever Kiss and Urmanczy transposed from natural logarithms to common logarithms, they multiplied the natural logarithm by the factor 2.303 instead of dividing as they should have done. Inasmuch as they were consistent in the use of this factor, their values for s and K agreed to within 0.1 per cent with those values found by us when the factor 2.303 was used correctly in transposing from the natural to the common system of logarithms.

the concentrations at equilibrium are:

$$c_{ClI_2^-},\ c_{BrI_2^-},\ \text{or}\ c_{I_3^-} = S - s$$

$$c_{Cl^-},\ c_{Br^-},\ \text{or}\ c_{I^-} = C - (S - s)$$

$$c_{I_2} = s$$

Then in terms of the mass action law, we have:

$$K_{c_{ClI_2^-}} = \frac{c_{I_2} \times c_{Cl^-}}{c_{ClI_2^-}} = \frac{(s)\ (C - S + s)}{(S - s)} \tag{3b}$$

and, similarly, for the two equilibria, BrI_2^- (3c) and I_3^- (3a).

The value for the activity coefficient, f, of a solute in a saturated solution is determined by the relationship (22):

$$\log \frac{s}{s_0} = \log \frac{f_0}{f} \tag{4}$$

where s and s_0 have the same significance as previously stated, and the characters with the subscript 0 refer to water at a pH of 5 as solvent, and those without the subscript refer to a solvent prepared by adding neutral salts to water and adjusting the pH to 5. There are two possible standard states of reference, namely, water and the solvent salt (23). In the first case, f_0, the activity coefficient of the saturating solute, iodine, in water is set equal to unity. In the second case, f, the activity coefficient of the saturating solute, iodine, in the salt solvent is set equal to unity.

Defining

$$K_c \times K_f = K_a \tag{5}$$

where K_c, K_f, and K_a represent the constants for the mass law expression in terms of concentrations, activity coefficients, and activities, respectively. In each case K_a is determined graphically by plotting the values of $K_{c_{ClI_2^-}}$ or of $K_{c_{BrI_2^-}}$ or of $K_{c_{I_3^-}}$ against the concentration of added halide, and extrapolating to zero concentration of added salt. K_a is a constant for any given temperature and pressure which is independent of the changes in concentration. K_a for any given equilibrium changes only as the solvent changes. Since in a solution saturated with iodine,

$$c_{I_2} \times f_{I_2} = a_{I_2} \tag{6}$$

a_{I_2} is a constant, the change in the values for K_c with the total salt concentrations is due largely to the variations in the ratios of $f_{\text{halide-iodine ion}}$ to

$f_{\text{halide ion}}$. This ratio of the activity coefficients of ClI_2^- to Cl^-, of BrI_2^- to Br^-, and of I_3^- to I^- may be calculated from

$$\frac{f_{ClI_2^-}}{f_{Cl^-}} = \frac{K_{c_{ClI_2^-}} \times f_{I_2}}{K_{a_{ClI_2^-}}} \tag{7b}$$

similarly, for the ratio of $f_{BrI_2^-}$ to f_{Br^-} (7c), and for the ratio of $f_{I_3^-}$ to f_{I^-} (7a). If these solubility measurements are made in concentrated salt solutions and if the ratio of the activity coefficients is determined solely by the electrical charge type, this ratio should be unity (24). Any deviations from unity must be due to specific individual properties of the halide ion as contrasted with the halide–iodine ion. That is, in solutions of high salt concentration, whereby the environment is held constant, a constant value for the mass action function, K_c, independent of the halide–iodine formation is a sufficient explanation for the increased solubility of iodine.

Discussion of the halide–iodine equilibria

The solubility of iodine was determined in a 1.65 molar and in a 2.0 molar potassium chloride solution. It is evident from column 5 of table 3 and from curve 3 of figure 2 that the value for $K_{c_{ClI_2^-}}$ increases slightly with increasing concentration of added halide ion. Kiss and Urmanczy's data substantiate this statement (figure 2, curve 1), but are not in quantitative agreement with these values.

This increasing value for the mass action function, K_c, signifies that as the chloride ion concentration increases, relatively less of the chloride ion combines with the iodine to form the chloride–iodine complex. This drift indicates either (a) that a different method of calculating the concentration of free iodine should be derived, (b) that the formation of a complex other than ClI_2^- ion should be considered, or (c) that the environment is not strictly constant, i.e., the simple gas laws are not obeyed.

This non-attainment of constant values for the $K_{c_{ClI_2^-}}$ expression is apparently in contradiction to data obtained experimentally by Carter and coworkers (25). The latter determined the solubility of iodine in different chlorides (potassium chloride, sodium chloride, barium chloride, etc.) of varying concentration and calculated the values for the $K_{c_{ClI_2^-}}$ function. Curve 4 of figure 2 records these values for sodium chloride as given by Dawson and Carter (25) and shows that practically constant values for $K_{c_{ClI_2^-}}$ are obtained. However, their method of calculating the salting-out constant for the chloride ion on iodine is such that the concentrations of iodine, chloride ion, and chloride–iodine ion complex are idealized, i.e., these values used are really activities and not concentrations.

This may be shown as follows: Carter and his associates did not consider

TABLE 3

Solubility of iodine in water to which two concentrations of potassium chloride were added

$k = 0.162$; $K_{a_{ClI_2^-}} = 0.629$; all solubilities are multiplied by 10^3

KCl ADDED	S	s	$c_{ClI_2^-}$	$K_{c_{ClI_2^-}}$	REFERENCE STATE	
					f_{I_2}	$\frac{f_{ClI_2^-}}{f_{Cl^-}}$
molar						
	1.321					
1 65	3.533	1.012	2.521	0.658	1.31	1 37
2.0	3.829	0.956	2.870	0.664	1.38	1.46

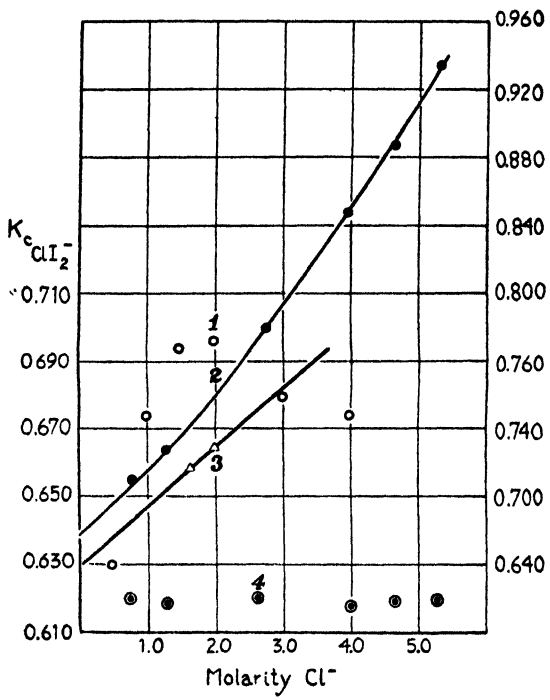

FIG. 2

○ Potassium chloride (Kiss and Urmanczy); ordinates on the left.
● Sodium chloride (Dawson and Carter, recalculated); ordinates on the right.
△ Potassium chloride (present investigation); ordinates on the left.
⊙ Sodium chloride (Dawson and Carter, original); ordinates on the left.

the salting-out effect,—they therefore assumed that the concentration of free iodine was equal to its concentration in water, and that the increase in the solubility of iodine on the addition of potassium chloride was due

entirely to the formation of ClI_2^- ion and they calculated the values for the mass action expression according to equation 3b. These values were then plotted against the concentration of added chloride ion and were extrapolated to $C = 0$ to obtain $K_{a_{ClI_2^-}}$ value, termed by these workers $K_{0_{ClI_2^-}}$. Mathematically this may be expressed as

$$\lim_{c_{Cl^-} \to 0} K_c = \lim_{c_{Cl^-} \to 0} \frac{c_{I_2} \times c_{Cl^-}}{c_{ClI_2^-}}$$

which has a definite value corresponding to an extrapolation of the constant to infinite dilution. This limit, which Carter calls $K_{0_{ClI_2^-}}$ is designated in the present notation as $K_{a_{ClI_2^-}}$. Carter and coworkers (25) combined the two subjoined equations to eliminate s,

$$K = \frac{(s)\ (C - S + s)}{(S - s)}$$

and

$$s = s_0 e^{-kC} \tag{2}$$

and assuming that $(S - s)$ is small as compared with C, and $K_{c_{ClI_2^-}}$ equal to $K_{a_{ClI_2^-}}$, they obtained the following approximation:

$$k = 1/C \log_e s_0\ (1 + C/K)/S$$

Thus they obtained the value for k (salting-out constant), and the value for s (concentration of free iodine) could then be calculated by the Setschenow equation (2).

Inasmuch as they set $K_0 = K_c$ in calculating the value for k (equation 2), and as this value was used to determine s, the concentration of free iodine—the most important factor, for at equilibrium the concentration of each substance is determined in part by this value—the values for k, I_2, ClI_2^- ion and Cl^- ion approximate ideally perfect ones, and the values reported for the mass law expression lose the significance intended for them.

The justification of the present reasoning and criticism is now presented and is independent of a statement made by Kiss and Urmanczy (5). Setting

$$x = c_{I_2} = s' \neq s_0$$

s' is used rather than s to avoid confusion, but it will be seen subsequently that $s' = s$ (Carter) $\neq s$ (Kiss and Urmanczy). Carter and his associates stated that

$$\frac{(x)\ (C - S + x)}{(S - x)} = K_c$$

whereas it is really K_a. For this value for K_c was found by plotting the concentration of added halide against the values obtained for the mass action expression, assuming $k = 0$ and extrapolating to $C = 0$ (previously described). Since x is the only unknown, the equation takes the quadratic form yielding,

$$x^2 + x\,(C - S + K_c) - K_cS = 0;\ x = \phi(CS).$$

For each concentration of added halide the value of x, the concentration of free iodine, is calculated and substituted in the Setschenow equation (2) to find the value for k. The value for k so derived is identical with that of Carter and coworkers as was expected. Thus the values for I_2, ClI_2^- ion, and Cl^- ion approximate activities rather than the desired concentration values.

TABLE 4

Solubility of iodine in 2.0 molar potassium nitrate to which three different concentrations of potassium chloride were added

k = 0 162; all solubilities are multiplied by 10^3

KCl ADDED	S	s	$c_{ClI_2^-}$	$K_{c_{ClI_2^-}}$	STATES OF REFERENCE		
					H_2O K_a = 0 629	2 M KNO_3 K_a = 0.628	
					f_{I_2}	f_{I_2}	f_{ClI_2}/f_{Cl}
molar							
	1 039				1 27	0 787	
0 05	1 112	1 031	0 0815	0 631	1 28	0 780	0 784
0 5	1 725	0.9583	0.7667	0 624	1.38	0.725	0 720
1 0	2 285	0 8839	1.4011	0 630	1 49	0 669	0 671

Curve 4 of figure 2 gives the values for $K_{c_{ClI_2^-}}$ function for sodium chloride as calculated by Dawson and Carter (25). The values for this function have been recalculated (using the salting-out constant as given by Kiss and Urmanczy) and have been plotted in figure 2, curve 2.

Since it is probable that changes in ionic environment are responsible for the deviations in these values for the mass law expression, the values for the $K_{c_{ClI_2^-}}$ function have been determined in the neutral salt solvent, 2 molar potassium nitrate. Table 4, column 5, shows that these values are practically invariant. Consequently, the assumptions that the only complex which need be considered is the ClI_2^- ion and that if the environment is stabilized then constant values for the $K_{c_{ClI_2}}$ function are obtained, are valid.

It will be noted (table 5, column 5, and figure 3), that in replacing a solution of potassium chloride by one of potassium bromide the values for the mass action function,

$$K_{c_{BrI_2^-}} = \frac{c_{I_2} \times c_{Br^-}}{c_{BrI_2^-}} \tag{3c}$$

decrease with increasing concentration of added halide, though in each case the environment has been stabilized with 2 M potassium nitrate. However, this drift in the value for the $K_{c_{BrI_2}}$ could have been predicted, for

TABLE 5

Solubility of iodine in 2.0 molar potassium nitrate to which six different concentrations of potassium bromide were added

k = 0.151; K_a = 0.0820 (water as standard state); K_a = 0 0759 (2 0 molar potassium nitrate as standard state); all solubility values are multiplied by 10^3

KBr ADDED	S	s	$c_{BrI_2^-}$	$K_{c_{BrI_2^-}}$	STATES OF REFERENCE			
					H_2O		2 0 M KNO_3	
					f_{I_2}	$\frac{f_{BrI_2^-}}{f_{Br^-}}$	f_{I_2}	$\frac{f_{BrI_2^-}}{f_{Br^-}}$
molar								
	1 039							
) 025	1 375	1 035	0 340	0 0752	1 27	1 17	0 783	0 776
) 05	1 717	1 031	0 696	0 0741	1 28	1 16	0 780	0 762
) 1079	2 508	1 022	1 486	0 0732	1 29	1 15	0 774	0 746
) 2	3 760	1 008	2 752	0 0722	1 31	1 16	0 763	0 726
) 5	7 741	0 9636	6 777	0 0701	1 37	1 17	0 729	0 673
0	14 06	0 8938	13 162	0 0670	1 48	1 20	0 677	0 598

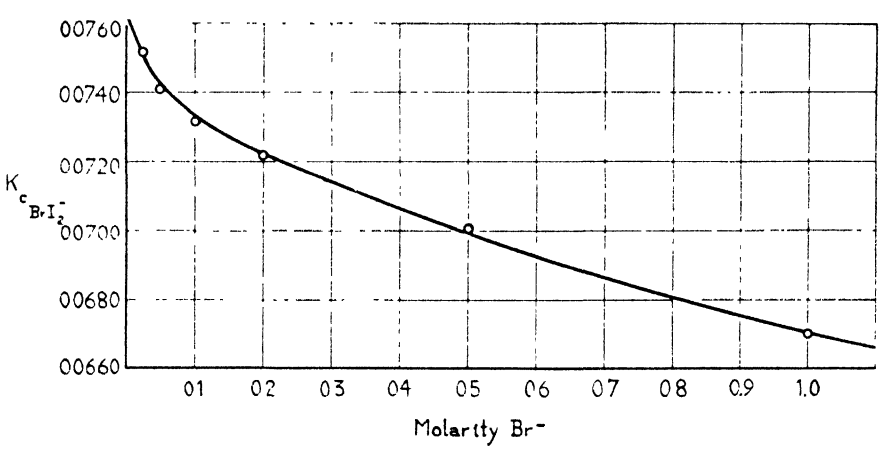

FIG. 3

the solubility of iodine is approximately 8.5 times as great in a potassium bromide solution as it is in a potassium chloride of the same molar concentration (table 11, columns 2 and 3). That this variation in the mass

law expression is due to the formation of a complex other than BrI_2^- ion and is not in contradiction to the Brönsted principle may be concluded from the following statements: In both potassium chloride and potassium bromide solutions the solubility of iodine increases almost linearly with the increasing concentration of added halide ion. Up to 0.5 molar, for the molarity of the potassium bromide solution there is a decrease in the mass action function of approximately 1.5 per cent, while as the concentration of potassium bromide is doubled (0.5 M to 1.0 M) the decrease in the $K_{c_{BrI_2}}$ value is 4.5 per cent. This indicates that as the concentration of added halide increases, the excess solubility of iodine in potassium bromide is due more and more to the formation of a complex other than BrI_2^-, probably BrI_4^-. Table 5, columns 7 and 9, shows how far variations in the activity coefficient ratio, $f_{BrI_2^-}/f_{Br^-}$, are responsible for this decrease in the mass action function.

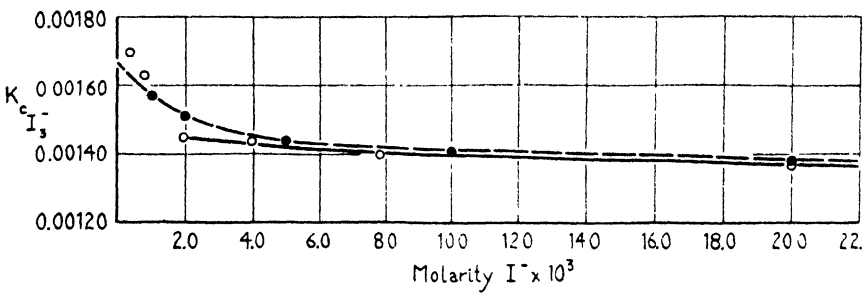

FIG 4

○ Sodium iodide (Carter (12)).

● Potassium iodide (Bray and MacKay (27)), $K_{a_{I_3^-}}$ is 0.00153; (Lewis and Randall (28)), $K_{a_{I_3^-}}$ is 0.00143 from these measurements

The study of addition complexes, i.e., BrI_2^- and ClI_2^- ions, resulted in part from that of the triiodide ion complex, which, without doubt, was the first halide–iodine equilibrium to be studied. From an exhaustive study of all pertinent literature, Grinnell Jones (26) has concluded that iodine does dissolve in a solution of an iodide ion to form the triiodide ion, and the value for the mass action function for this equilibrium decreases with increasing concentration of added halide ion.

To substantiate this statement there has been included the data of Bray and MacKay (27) and of Carter (12) (figure 4, curves 1 and 2). Bray and MacKay gave a value of 0.00153 for the K_a representing the triiodide equilibrium. Jakowkin (13) from distribution measurements and Grinnell Jones (29) from solubility measurements gave 0.00140 as the value for this equilibrium. This value has been used throughout the present calculations as K_a to evaluate the ratio of the activity coefficients of the triiodide

to the iodide ion when water is chosen as the reference state, according to equation 7.

Although the triiodide equilibrium has been investigated in considerable detail, it has received little attention in neutral salt solvents. Values for

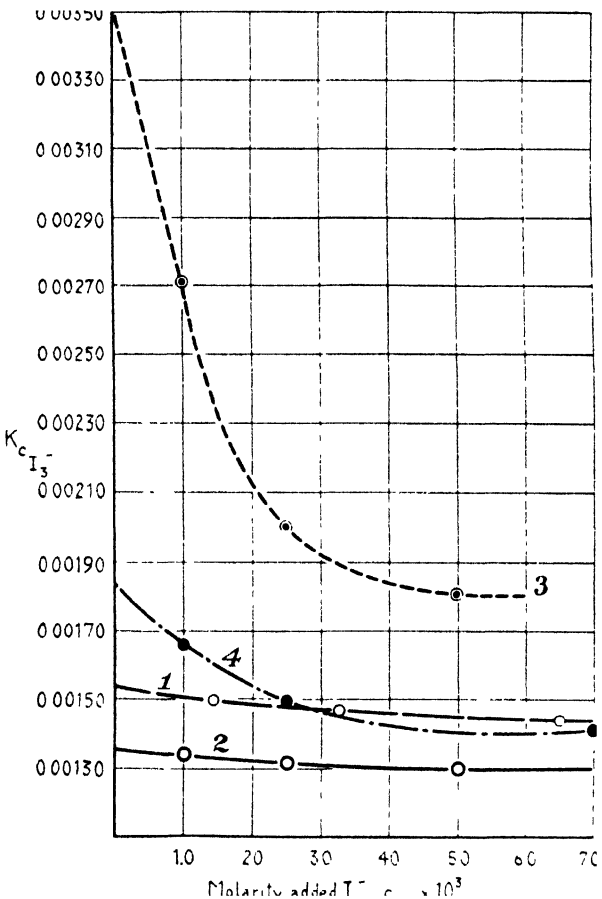

FIG. 5

○ 1.698 *M* sodium sulfate as solvent (Carter).
o 2.0 *M* potassium nitrate as solvent.
⊙ 2.0 *M* potassium chloride as solvent.
● 2.0 *M* potassium nitrate plus 1.0 *M* potassium chloride as solvent.

the equilibrium function are often needed for such solvents, and should be in closer agreement, for the environment is constant, than they are in water as solvent, though perhaps decreasing slightly with increasing concentration of the halide ion, as postulated by Bronsted.

Carter (12) used 1.698 molar sodium sulfate as the neutral salt solvent to which sixteen different concentrations of sodium iodide were added, and then through solubility measurements calculated the values for $K_{c_{I^-}}$ expression. From this data there have been computed the values for the

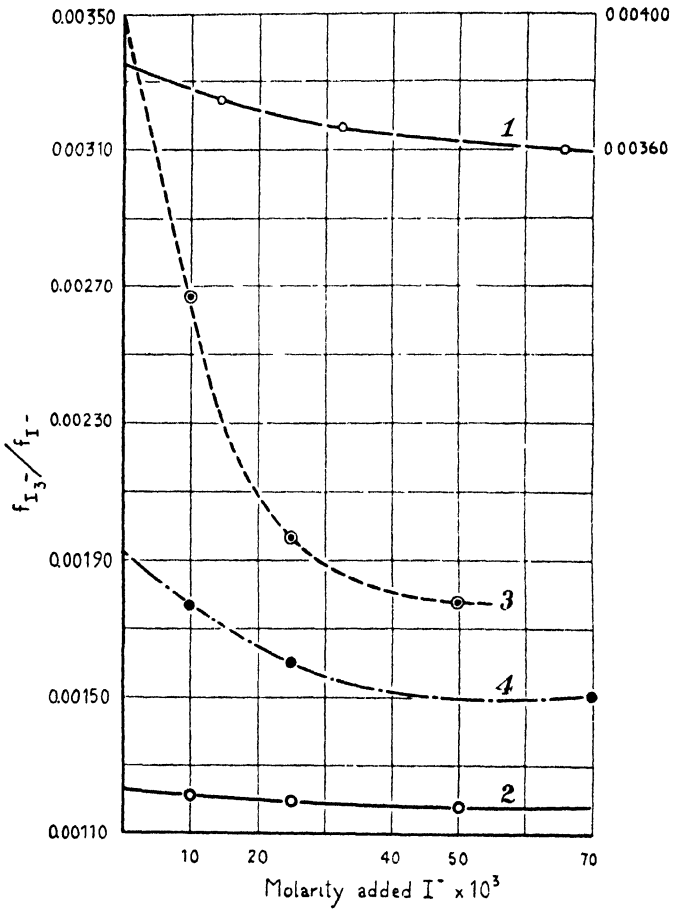

FIG. 5a

○ 1.698 *M* sodium sulfate as solvent (Carter).
o 2.0 *M* potassium nitrate as solvent.
⊙ 2.0 *M* potassium chloride as solvent.
● 2.0 *M* potassium nitrate plus 1.0 *M* potassium chloride as solvent.
Ordinates on the left are for curves 2, 3, and 4; ordinates on the right for curve 1.

ratio of $f_{I_3^-}/f_{I^-}$. These values (figures 5 and 5a, curve 1) show a decided downward drift with increasing concentration of added iodide ion.

A solution of 2.0 molar potassium nitrate was preferred to one of sodium sulfate, as the solvent maintaining constant ionic environment for the

nitrate ion is known to have a salting-out effect 2.2 times smaller than the sulfate ion has. In neither case was it necessary to calculate the concentration of free iodine considering the salting-out effect of the sulfate ion or of the nitrate ion on iodine, for here the concentration of free iodine would not change the numerical value of the more important ratio of c_{I^-} to c_{I_2}. Therefore, the per cent drift in the value for $K_{c_{I_3^-}}$ should be the same, although the numerical value would be altered slightly. The salting-out effect of the iodide ion on iodine was ignored.

It is evident from table 6 (columns 5, 7, and 9) and curve 2 of figures 5 and 5a that the values for the $K_{c_{I_3^-}}$ function and those for the ratio f_{I_2}/f_{I^-} decrease very slightly with increasing concentration of added iodide ion. However, it must be pointed out that the values for the equilibrium expression, when 2.0 molar potassium nitrate is used as solvent, are more

TABLE 6

Solubility of iodine in 2.0 molar potassium nitrate to which four different concentrations of potassium iodide were added

K_a = 0.00135 (2.0 molar potassium nitrate as standard state); K_a = 0.00140 (water as reference state); all solubility values are multiplied by 10^3

KI ADDED	S	s	c_{I_2}	$K_{c_{I_3^-}}$	STATES OF REFERENCE			
					H_2O		2.0 M KNO_3	
					f_{I_2}	$f_{I_3^-}/f_{I^-}$	f_{I_2}	$f_{I_3^-}/f_{I^-}$
molar								
	1.039				1.27		0.787	
0.001	1.475	1.039	0.436	0.00134	1.27	1.215	0.787	0.799
0.0025	2.139	1.039	1.1	0.00132	1.27	1.20	0.787	0.771
0.005	3.256	1.039	2.217	0.00130	1.27	1.18	0.787	0.763
0.02	9.945	1.039	11.09	0.00129	1.27	1.17	0.787	0.756

nearly constant on varying the concentration of added iodide ion, than are the values when either water or 1.698 molar sodium sulfate is used as solvent.

In their recent publication Kiss and Urmanczy (5) made the tacit assumption that the triiodide equilibrium is the only one involved to account for the increase in the solubility of iodine on the addition of dilute solutions of iodide ion to neutral salts used as solvents, whereby the environment is stabilized. These authors used only one concentration of potassium iodide (0.025 M) added to the solvent salt, and consequently ignored the possibility that there might be a drift in the values for the $K_{c_{I_3}}$ function. Their value for the $K_{c_{I_3}}$ function is 0.00130 in 2.0 molar potassium nitrate as solvent. However, it is evident from the values obtained in the course of this investigation for the mass law expression, which decrease from 0.00134 to 0.00129 as the concentration of added iodide ion increases from

0.001 to 0.01 molar, that their unproven assumptions, i.e., that the triiodide is the only important polyiodide and that the salting-out effect of the iodide ion on the iodine molecule may be discounted, are valid for solvents, like potassium nitrate, sodium sulfate, etc., which salts give no evidence of combining chemically with the iodine.

Several authors (30) have assumed that regardless of the salt used as solvent to stabilize the environment, the value for the mass action function $K_{c_{I_3^-}}$ shall be invariant. Therefore, two different concentrations of potassium chloride were used as solvent, namely, 1.65 and 2.0 molar, to which three different concentrations of potassium iodide were added in each of which the solubility of iodine was determined.

For each, the chloride–iodine complex and only the salting-out effect on the chloride ion on the iodine were considered, as suggested by Carter (4), but calculated according to the method of Kiss and Urmanczy (5). It

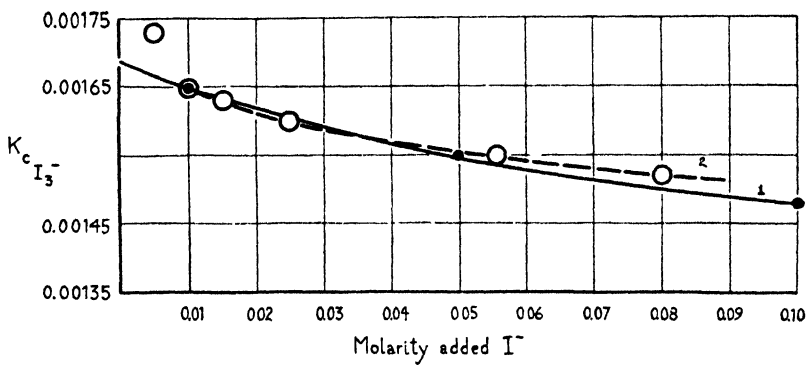

FIG. 6

● Present investigation.
○ Spivey and Dawson.

is evident from figures 6 and 5 (curves 1 and 3, respectively), and tables 7 and 9 (column 5) that these data are in contradiction to the current idea. The work of Spivey and Dawson (30), which appeared after the completion of the experimental work for potassium chloride as solvent here reported, substantiates these values for the mass action expression representing the triiodide equilibrium. Curve 2 of figure 6 records the data of Spivey and Dawson.

It was for this solvent, namely, 1.65 molar potassium chloride, that Brönsted and Pedersen (1) gave an extrapolated value for the $K_{a_{I_3^-}}$ at 25°C., called "*L*," as 0.00611. This value, correcting for the chloride–iodine complex and the salting-out effect of chloride ion on iodine, has been recalculated and found to be 0.00175, which agrees with the mean value of Spivey and Dawson (30) and that obtained by the present investigators.

Spivey and Dawson (30) in their calculations used the value for the salt-

ing-out constant k for the chloride ion on iodine as determined by Carter (4), to calculate the concentration of free iodine,—a procedure, which as previously pointed out, is questionable. In table 8, columns 3, 6, and 4, 7 show that this error is unimportant in this particular case. The more important factor in calculating the value for the $K_{c_{I_3^-}}$ relationship is that the ratio of c_{I^-} to c_{I_2} shall be constant, and not whether the salting-out effect of the chloride ion on iodine has been correctly considered. The

TABLE 7

Solubility of iodine in 1.65 molar potassium chloride to which three different concentrations of potassium iodide were added

k = 0 162; K_a = 0.00168 (solvent as reference state)

KI ADDED	S	s	$c_{I_3^-}$	$K_{c_{I_3^-}}$	STATES OF REFERENCE			
					H_2O		1 65 M KCl	
					f_{I_2}	$f_{I_3^-}/f_{I^-}$	f_{I_2}	f_{I^-}/f_{I^-}
molar								
	3.533	1 012			1 30		0 766	
0 01	7 335	1 012	3.802	0 00165	1 30	1 54	0 766	0 757
0 05	23 32	1 012	19 78	0 00155	1.30	1 45	0 766	0 707
0 1	44 203	1 012	40.67	0 00148	1 30	1 37	0.766	0 675

TABLE 8

Comparison of the values for the $K_{c_{I_3^-}}$ expression in a 1.65 molar potassium chloride solution as solvent (obtained by Spivey and Dawson) with those in table 7

k = 0.172 (Spivey and Dawson); k = 0.162 (table 7)

The former's values were recalculated using k = 0.162

KI ADDED	s (TABLE 7)	SPIVEY AND DAWSON		$K_{c_{I_3^-}}$ (TABLE 7)	SPIVEY AND DAWSON	
		k = 0 172 s	k = 0 162 s		k = 0 172 $K_{c_{I_3^-}}$	k = 0 162 $K_{c_{I_3^-}}$
molar						
0 01	1 012	0 994	1 012	0 00165	0 00165	0 00168
0 05	1 012	0 994	1 012	0 00155		
0 056	1 012	0 994	1 012		0 00155	0 00157
0 08	1 012	0 994	1 012		0 00152	0 00154
0 1	1 012	0 994	1 012	0 00148		

latter merely changes the numerical value of $K_{c_{I_3^-}}$ and does not here make for constancy of results. Therefore, this decided drift in the value of the constant for the mass law equilibrium probably is due to a factor other than the salting-out effect of the chloride ion on iodine.

There are three other possible reasons for the non-attainment of invariant values for the mass law expression representing the triiodide equilibrium in a chloride ion solvent.

(1) Probable failure of the Brönsted principle: If 2.0 molar potassium nitrate is a sufficiently concentrated solution to stabilize the environment, then the same should be true for 2.0 molar potassium chloride. To show that this failure to obtain constant values for the $K_{c_{I_3^-}}$ expression does not represent a failure, but rather a misinterpretation of the Brönsted principle, 2.0 molar potassium nitrate plus 1.0 molar potassium chloride

TABLE 9

Solubility of iodine in 2.0 molar potassium chloride to which three different concentrations of potassium iodide were added

$k = 0.162$; $K_a = 0.00140$ (water as reference state); $K_a = 0.0034$ (2.0 molar potassium chloride as reference state); all solubilities are multiplied by 10^3

KI ADDED	S	s	$c_{I_3^-}$	$K_{c_{I_3^-}}$	STATES OF REFERENCE			
					H_2O		2 0 M KCl	
					f_{I_2}	f_{I_3}/f_{I^-}	f_{I_2}	f_{I_3}/f_{I^-}
molar								
	3.829	0 956			1 37		0 725	
0 001	4 090	0.956	0 261	0 00271	1 37	2.67	0 725	0.576
0.0025	4 638	0 956	0 809	0 00200	1.37	1 97	0 725	0.425
0 005	5 560	0.956	1 731	0 00181	1.37	1.78	0.725	0.389

TABLE 10

Solubility of iodine in 2.0 molar potassium nitrate plus 1.0 molar potassium chloride to which three different concentrations of potassium iodide were added

$k = 0.162$; $K_a = 0.00184$ (solvent as reference state); $K_a = 0.00140$ (water as reference state); all solubilities are multiplied by 10^3

KI ADDED	S	s	$c_{I_3^-}$	$K_{c_{I_3^-}}$	STATES OF REFERENCE			
					H_2O		Solvent	
					f_{I_2}	f_{I_3}/f_{I^-}	f_{I_2}	f_{I_3}/f_{I^-}
molar $\times 10^3$								
	2 285	0 882			1.50		0 668	
1 0	2 632	0 882	0 3467	0 00166	1 50	1.77	0 668	0.603
2 5	3.212	0.882	0 9274	0 00150	1 50	1 60	0.668	0.545
6 956	4.963	0.882	2 678	0.00141	1.50	1 51	0 668	0.512

was selected as solvent. In this solvent the values for the mass law expression and the ratio of the activity coefficients of the triiodide ion to the iodide ion follow the same drift, but to a less extent than they did in 2.0 molar potassium chloride solvent (figures 5 and 5a, curves 4 and 3). Table 10 cites the afore-mentioned values for this mixed solvent. Equivalent concentrations of potassium iodide were added. This indicates that the Brönsted principle must be carefully interpreted, i.e., a salt employed as solvent must be chemically inert with respect to the other solutes.

(2) Formation of higher polyiodides. Heretofore this served as the answer. Similarly, Spivey and Dawson (30) ascribed this marked decrease in the values of the $K_{c_{I_3^-}}$ function to the formation of small quantities of I_5^- ion. The values for the $K_{c_{I_3}}$ function in solvents, potassium nitrate and sodium sulfate, show that the amount of I_5^- ion formed depended only upon the concentration of added iodide ion. Should one not then expect that the amount of I_5^- ion formed for a definite concentration of added iodide ion be independent of the salt used as solvent? But this is not true. From the summary of the concentrations of the triiodide ion formed on the addition of equivalent amounts of iodide ion in the three solvents,

TABLE 11

Comparison chart

2 0 molar potassium nitrate as solvent

ADDED HALIDE	$c_{ClI_2^-}$	$c_{BrI_2^-}$	$c_{I_3^-}$	$K_{c_{ClI_2^-}}$	$K_{c_{BrI_2^-}}$	$K_{c_{I_3^-}}$
molar						
0 05	0 000083			0 6321		
0 025		0 00034			0 0752	
0 001			0 000436			0 00134
0 05		0 000686			0 0742	
0 5	0 000769			0 6244		
0 0025			0.0011			0 00132
1 0	0 001403			0 6299		
0 1079		0 001486			0 0732	
0 005			0 002217			0 00130
0 2		0 002753			0 0722	
0 5		0 006775			0 0701	
0 02			0 008907			0 00129
1 0		0 01316			0 0670	
K_a values . .				0 628	0 0759	0 00135

as presented in figure 7, it is evident: first, that the concentration of the triiodide ion formed decreases markedly with increasing molarity of added potassium chloride; secondly, that when potassium nitrate is present as solvent the values for the $K_{c_{I_3}}$ function are more nearly constant; and third, that whenever potassium chloride is present in the solvent the drift in the $K_{c_{I_3}}$ expression follows the same course (figure 5). Therefore, it is necessary to consider another hypothesis as an explanation for this drift in the values of the mass law expression representing the triiodide equilibrium in the presence of potassium chloride.

(3) Salting-out of ions on ions. It is evident from figure 7 that as the chloride ion concentration is increased, the amount of the triiodide ion formed on the addition of equivalent molarities of potassium iodide is

markedly decreased. The chloride ion or the chloride–iodine ion complex must have exercised a salting-out effect on the iodide ion whereby the concentration of the triiodide ion would be lessened. Unfortunately there is at the present time no adequate method (31) of calculating the salting-out effect of ions on ions. It must be sufficient to state that the salting-out effects of the chloride ion and the nitrate ion on the iodide ion are different, the effect of the latter being small in comparison with the chloride ion.

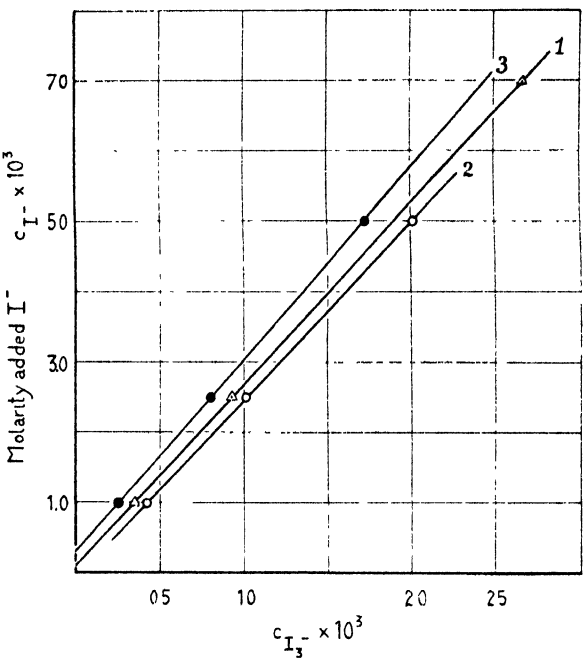

FIG. 7

● 2.0 *M* potassium chloride as solvent.
△ 2.0 *M* potassium nitrate plus 1.0 *M* potassium chloride as solvent.
⊙ 2.0 *M* potassium nitrate as solvent.

Therefore, the non-attainment of constant values for the $K_{c_{I_3^-}}$ expression in a solvent of constant but high chloride ion content appears to be due to a large salting-out effect of the chloride ion or of the chloride–iodine ion complex or of both on the iodide ion and not (a) to the changing environment produced by the addition of small concentrations of potassium iodide to the salt solvent, or (b) to the incorrect values for the salting-out constant for the chloride ion on the neutral molecule, iodine. Thus the concentration of the triiodide ion is small as compared with its value if the

chloride ion exercises no salting-out effect on the iodide ion, and therefore the values for the mass action function representing the triiodide equilibrium in a chloride ion solvent here reported are high.

However, it is just possible that if one reads into the assertion made by Carter and Hoskins (4), the thought that the mutual salting-out effect of ions on ions must be considered, then constant values for the mass law expression representing the triiodide equilibrium may be obtained, regardless of the salt employed as solvent maintaining a constant ionic environment.

IV. SUMMARY

1. The solubility of iodine at 25°C. in water at a pH of 5, to prevent hydrolysis, has been established as 0.001321 $\pm 2 \times 10^{-6}$ moles per liter of solution.

2. The values for the mass action expressions for the three equilibria:

EQUILIBRIA	CONSTANTS FOR THE EQUILIBRIA IN	
	H_2O	2 M KNO_3
$ClI_2^- \rightleftharpoons I_2 + Cl^-$	0.629	0.628
$BrI_2^- \rightleftharpoons I_2 + Br^-$	0.0820[5]	0.0759
$I_3^- \rightleftharpoons I_2 + I^-$	0.00140	0.00135

are more nearly constant with changing halide concentration in the presence of 2 M potassium nitrate than in water. Potassium nitrate gives no evidence of combining chemically with iodine and is used to maintain constant ionic environment.

3. Values for the expression for $K_{c_{I_3}}$ deviate considerably from the $K_{a_{I_3}}$ value in a potassium chloride solution, a salt which maintains a constant ionic environment but reacts chemically with iodine. This indicates that the assertion made by Carter and Hoskins is neither correct nor complete.

4. In a solvent containing potassium chloride, to which small amounts of potassium iodide were added, the values for the expression for $K_{c_{I_3^-}}$ are more nearly constant in the presence of potassium nitrate than in its absence.

[5] Bell and Buckley (32) determined the solubility of iodine in solutions of potassium and sodium bromides, but did not attempt a quantitative interpretation. The values for the mass action function have been calculated and the value for K_a for potassium bromide has been found by extrapolation. The latter value is incorporated in the summary.

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THE HYDROLS

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Liquid water is recognized as being more or less polymerized (7), but very little use is made of this except to account for the temperature of maximum density of water and for its not boiling at 80–193°K. as calculated by van't Hoff, Walden, Tammann, and Sidgwick. In many thermodynamical reasonings the assumption is made tacitly that the degree of polymerization does not change. Very few people are interested in the probability of the different forms of liquid water having different properties. This is the more remarkable because we are quite used to marked changes with different metamers and polymers.

We have red NO_2 and colorless N_2O_4; soluble and insoluble sulfur; anthracene and dianthracene; red phosphorus and white phosphorus; diamond and graphite; cyanic acid, cyanuric acid, and cyamelid; acetaldehyde and paraldehyde; oxygen and ozone; ordinary and nascent hydrogen, oxygen, and nitrogen. The enol and keto forms can be distinguished. Polymerized alcohol peptizes pyroxylin while depolymerized alcohol does not. The two forms of chromic chloride and of benzaldoxime each lower the melting point of the other. The dielectric constant of solid nitrobenzene I is nearly four times that of solid nitrobenzene II.

The lyotropic or Hofmeister series of chloride, bromide, and iodide is found to hold both for true solutions and for colloidal solutions. In the case of true solutions the series holds for reaction velocity experiments (neutral salt effect), electromotive forces, boiling points, and displacements of the temperature of maximum density. Sodium chloride increases the dissociation constant (18) of carbonic acid one thousandfold. Sodium chloride increases the apparent strength of boric acid (16). The apparent molecular weights of sodium chloride, bromide, and iodide vary in that order. The potential difference between hydrogen and hydrochloric acid differs from that between hydrogen and hydrobromic acid (26). Richards and Rowe (19) found that the heats of neutralization of caustic soda and caustic potash decrease as the neutralizing acid changes from hydrochloric acid to hydrobromic acid and then to hydriodic acid. The solubility of gases in salt solutions, the heat capacity of water, the displacement of the temperature of maximum density of water, and the quenching of fluorescence in certain solutions by salts show the same general phenomenon.

The Hofmeister series holds in colloidal solutions for the peptization and precipitation of proteins, cellulose, and many other colloids. We do not at present consider adsorption as occurring in true solutions, though the conception of a water sheath on ions is practically adsorption. So long as we adopt the ordinary point of view, adsorption is not a necessary cause of the Hofmeister series. The Hofmeister series cannot be due to electrostatic effects because nitrates are very different from chlorides and bromides, though coming between them in molecular weights. It cannot be due to hydrated or hydrous ions because the boiling points are more abnormal than the freezing points and also because on that hypothesis hydrous or hydrated iodides should raise the setting points of gelatin jellies and should increase the rate of saponification of esters. The neutral salt effect cannot be due to an increased dissociation of the acid, because it is easy to get effects corresponding to many times 100 per cent dissociation. Many people have suggested an increased dissociation of water, but no one has maintained it seriously for any length of time. Sodium chloride alone does not invert sugar solution at an appreciable rate. Sodium chloride, bromide, and iodide decrease the rate of saponification of methyl acetate.

The only thing that is left is that the Hofmeister series is due in part to a change in the degree of polymerization of water (1). For the cases in which one can eliminate adsorption, the neutral salt effect is due exclusively to a change in the water equilibrium. For other cases selective adsorption may play the important part. With gelatin the order of effectiveness of the anions is the same on both sides of the isoelectric point and the amounts of chloride or iodide adsorbed are so small that nobody has ever measured them in aqueous solutions. With gelatin the change in the water equilibrium is the important one, and the effect due to adsorption of the anion is practically negligible for chlorides, bromides, and iodides, though it does exist. With albumin the order of the effectiveness of the anions reverses as one changes from acid to alkaline solutions. Here the adsorption is the important factor and the displacement of the water equilibrium is of much less importance. Gelatin and albumin may be taken as representing the two extremes. Hofmeister (11) deduced the Hofmeister series from experiments on proteins.

Since adsorption is selective, the order of the anions will not necessarily be the same in all cases and colloid chemists know that the Hofmeister series varies somewhat with different adsorbents, nitrate jumping around in an especially disturbing way. It has not yet been shown that all these cases are due to differences in selective adsorption, but that will come in time. We have already proved it for the two cases that we have studied. The boiling point curve for sodium thiocyanate is more nearly normal than that for sodium iodide, whereas sodium thiocyanate peptizes gelatin more strongly than does sodium iodide. By using 80 per cent and 95 per cent

alcohol it was possible to show that sodium thiocyanate is adsorbed more strongly than sodium iodide. A similar explanation holds for sodium nitrate and sodium chloride. The nitrate has the more normal boiling point curve, peptizes gelatin a little better, and is adsorbed by gelatin more strongly.

The usual order of the anions in the Hofmeister series when adsorption is negligible is I^-, SCN^-, Br^-, NO_3^-, Cl^-, SO_4^{--}. When selective adsorption occurs, a common order is SCN^-, I^-, Br^-, NO_3^-, Cl^-, SO_4^{--}.

We have introduced a set of arbitrary assumptions for the effects of these six ions on water. This will make the discussion more definite and should be helpful.

1. Under ordinary conditions liquid water may be considered as essentially a mixture of trihydrol (or polyhydrols), dihydrol, and monohydrol coëxisting in reversible equilibrium.

2. Chloride, bromide, thiocyanate, and iodide ions tend to change dihydrol into monohydrol and have no especial effect on trihydrol beyond that which is a necessary consequence of the displacement of the equilibrium between dihydrol and monohydrol. The order of increasing effectiveness is chloride, bromide, thiocyanate, and iodide.

3. The nitrate ion tends to convert trihydrol into dihydrol, and dihydrol into monohydrol. For equivalent concentrations the amount of monohydrol is less with nitrate ion than with chloride ion.

4. The sulfate ion tends to convert trihydrol and monohydrol into dihydrol.

5. The electrolytic solution pressure of hydrogen is greater in dihydrol than in monohydrol, and that of oxygen is less.

Many years ago Kahlenberg (14) showed that potassium iodide gave a greater rise of boiling point than potassium bromide, and potassium bromide a greater rise than potassium chloride. He also showed that these results were distinctly more abnormal than those with potassium nitrate. We have confirmed and extended his results. The experiments were made at 760 mm. with the arrangement of the Davis-Brandt apparatus (8), which permits working at constant pressure irrespective of fluctuations in barometric pressure. The data obtained with this apparatus are given in table 1. The concentration of the solutions is expressed in moles of the solute per kilogram of water. By plotting molal concentrations against rise of boiling points, we eliminate all question of the applicability of any particular formula. One reason why Kahlenberg's results were ignored was because he calculated molecular weights and people said that the formula did not hold for such concentrations. The solutions of sodium chloride, sodium bromide, sodium iodide, and sodium thiocyanate were titrated with standard silver nitrate solution, using potassium chromate as an indicator. The solutions of sodium nitrate were analyzed gas-

volumetrically with a Dennis nitrometer. The sodium sulfate solutions were determined by precipitating and weighing as barium sulfate.

TABLE 1

Boiling point data at 760 mm.

SALT	MOLES PER KILOGRAM OF WATER	RISE OF BOILING POINT	BOILING POINT RISE PER MOLE
		degrees C	*degrees C.*
NaCl	4 404	5 16	1 17
	2 070	2 04	0 985
	1 456	1 38	0 948
	0 889	0 79	0 888
	0 382	0 34	0 895
NaBr	3 896	4 73	1 21
	1 932	2 01	1 04
	0 687	0 63	0 918
	0 272	0 26	0 954
NaI	3 875	5 15	1 33
	2 398	2 73	1 14
	2 043	2 21	1 08
	1 910	2 04	1 07
	1 010	1 01	1 00
	0 588	0 55	0 935
$NaNO_3$	4 04	3 65	0 903
	3 01	2 70	0 897
	1 81	1 69	0 935
	0 926	0 85	0 918
	0 547	0 53	0 970
NaSCN	4 28	5 25	1 22
	3 01	3 38	1 12
	1 96	2 07	1.06
	0 93	0 92	0 980
	0 75	0 73	0 974
Na_2SO_4	2 70	2 55	0 945
	2 09	1 99	0 952
	1 37	1 34	1 01
	0 892	0 90	1.01
	0 476	0.50	1 05
	0 232	0.26	1 12

In dilute solutions the results for all salts fall practically on the same line, as they should. In more concentrated solutions the curves diverge. These results do not check those of Johnston (13) for the sodium bromide

solutions. His error is probably due to superheating, giving too high a boiling point.

There is a very real difference between such similar salts as sodium chloride and sodium iodide. At about 4 molal the rise of boiling point for sodium chloride is about 85 per cent of that for sodium iodide. This is a difference of about 0.7°C., which is far beyond the estimated experimental error of 0.03°C. There cannot be any such difference in dissociation. The difference cannot be due to adsorption in the ordinary sense of the word, because the salts are in true solution. Even at 3 normal the difference between sodium iodide and sodium nitrate is about 1°C.

Sidgwick and Ewbank (22) deduce from freezing point data that the lowering of the freezing point varies with the hydration of the ions. A similar conclusion has been drawn by Fajans and Karagunis (9). The difficulty with this is that in general the boiling points are more abnormal than the freezing points, whereas the degree of hydration must be greater at 0° than at 100°C., because the formation of hydrates is an exothermal process.

Arbitrary assumption No. 2 was based on the boiling point data. Iodides have the highest boiling points and then come thiocyanates, bromides, and chlorides. The differences between sodium thiocyanate and sodium bromide are very small. If iodides are the most effective in converting dihydrol into monohydrol, they are more soluble in monohydrol than in dihydrol and are consequently lowering the vapor pressure of the more volatile constituent. Therefore the rise of boiling point is abnormally large.

The temperature of maximum density of water is lowered by most salts. That means that these salts depolymerize water to some extent, thereby making it necessary to cool more before the expansion due to increased polymerization overbalances the contraction due to temperature contraction. On this basis iodide should have more effect than bromide and bromide more effect than chloride. This is the case. Unfortunately nitrate is more effective than iodide and sulfate more so than nitrate. Arbitrary assumptions Nos. 3 and 4 take care of the apparent exceptions.

Arbitrary assumption No. 5 is made to account for the apparent increase in concentration of hydrogen ion on addition of sodium chloride, bromide, or iodide to a solution of an acid. There can be no such change in concentration as there appears to be, and consequently the observed change in electromotive force must be due to a change in the so-called solution pressure. It would be much better if people would evaluate singly as many of the disturbing factors as possible instead of lumping them all under the purely formal term of activity.

As has been stated, the boiling points for sodium iodide are more abnormal than those for sodium thiocyanate, and the boiling points for sodium

chloride are more abnormal than those for sodium nitrate. On the other hand, sodium thiocyanate is a better peptizing agent for gelatin than sodium iodide, and sodium nitrate than sodium chloride. It was therefore necessary to show that gelatin adsorbs thiocyanate somewhat more strongly than sodium iodide, and sodium nitrate more strongly than sodium chloride. Previous experiments at Cornell and elsewhere had shown the practical impossibility of getting the necessary data with water as solvent. The experiments were therefore made in alcoholic solutions in which the peptization of gelatin and the adsorption of alcohol by gelatin are practically negligible.

TABLE 2

Adsorption by gelatin

SALT	SOLVENT	MOLES PER LITER IN SOLUTION	MILLIMOLES ADSORBED PER GRAM OF GELATIN
NaSCN	95 per cent alcohol	0 0592	0 171
		0 040	0 123
		0 0173	0 059
		0 0059	0 020
NaI	95 per cent alcohol	0 0805	0 193
		0 0504	0 139
		0 0240	0 063
		0 0086	0 030
NaCl	80 per cent alcohol	0 0554	0 291
		0 0410	0 215
		0 0236	0.115
		0 0060	0 023
$NaNO_3$	80 per cent alcohol	0 0558	0 303
		0.0385	0.212
		0.0225	0.121
		0 0058	0 028

Three grams of Eastman's de-ashed gelatin was used as obtained, adding 35 cc. of the alcoholic solutions. Sodium thiocyanate and sodium iodide were dissolved in 95 per cent alcohol; since sodium nitrate and sodium chloride are less soluble, 80 per cent alcohol was used for them. Trial runs showed that it was necessary to wait thirty-six hours in order to be sure of reaching equilibrium. At the end of that time 25 cc. of the supernatant liquid was titrated with a known silver nitrate solution, using potassium chromate as indicator. The data are given in table 2.

The results show that sodium thiocyanate is adsorbed more strongly by gelatin than sodium iodide is, and that sodium nitrate is adsorbed more

strongly than sodium chloride. There is therefore no necessary reason why the order of peptization should be identical with the order of boiling points.

Bowe (5) has used the theory of the water equilibrium to explain the neutral salt effect. If neutral salts cause a shift in the water equilibrium, we then have different solvents in which solubilities, reaction velocities, and degrees of ionization may be different from those in the original solvent. He showed that the equation for the electromotive forces postulates the constancy of the solution pressure of hydrogen. This is not true experimentally for hydrochloric acid, hydrobromic acid, and hydriodic acid.

Bowe showed that the addition of sodium chloride, sodium bromide, and sodium iodide to 0.1 *N* hydrochloric acid increased the apparent concentration of hydrogen ion in each case, the increase being greatest for sodium iodide and least for sodium chloride. Making the solution 4 normal with respect to sodium iodide increased the apparent concentration of hydrogen ion tenfold. To account for the facts we postulate that the solution pressure of hydrogen is less in monohydrol than in dihydrol. All determinations of hydrogen-ion concentration in halide solutions are therefore in error to some extent. Since all determinations of pH in biological systems are made in the presence of chlorides, all these determinations are in error to some extent, unless some other unsuspected error counteracted the first one.

These experiments suggested an even more striking one. The cell $H_2 \mid HCl \mid KCl\ \underline{Hg_2Cl_2} \mid Hg$ should have a higher electromotive force than the cell $H_2 \mid HBr \mid KCl\ \underline{Hg_2Cl_2} \mid Hg$, provided the molal concentrations of hydrochloric acid and hydrobromic acid are the same. The corresponding cell with hydriodic acid should have the lowest electromotive force of the three.

The electromotive forces of these three cells were measured, using a saturated calomel half-cell. After the electromotive forces had been determined, the solutions were analyzed volumetrically by titration with silver nitrate, using potassium chromate as indicator. It was not possible to run up to high concentrations of hydriodic acid, because under ordinary conditions iodine is set free and poisons the electrode. The results are given in table 3.

With strong acids of the same type, such as these, the percentage dissociation should not differ appreciably. The migration velocities are practically identical. At 8 normal concentration the difference between hydrochloric acid and hydrobromic acid is about 40 millivolts, which is far beyond the experimental error and which must therefore be due to a difference in solution pressure. These results agree with those of Wilke and Schränkler (26), who measured the cell $H_2 \mid HCl \mid HX \mid H_2$.

From a consideration of the boiling points of salt solutions and from the displacement of the water equilibrium by salts, we deduced (arbitrary assumption No. 4) that the sulfate ion tends to convert trihydrol and monohydrol into dihydrol. In this reaction heat is evolved, which accounts for the fact that the solubility curve for anhydrous sodium sulfate shows a decreasing solubility with rising temperature along the first part of this curve. The heat of formation of sodium sulfate decahydrate is sufficient to change the sign of the heat of solution, and consequently this salt shows an increasing solubility with rising temperature. At higher temperatures the effect of sodium sulfate in displacing the water equilibrium will probably become less, and therefore there may come a temperature at which this heat effect will just equal the algebraic sum of the heat of fusion plus the heat of dilution not due to displacement of the water equilibrium. At this temperature anhydrous sodium sulfate will have a minimum solubility. Experimentally the solubility curve for anhydrous sodium sulfate does

TABLE 3

Electromotive forces

$H_2 \mid HX \mid \underline{KCl}, \underline{Hg_2Cl_2} \mid Hg$

ACID	NORMALITY	E M F	ACID	NORMALITY	E M F
HCl	1 148	0 237	HBr	1 09	0 233
	2 900	0 215		2 06	0 212
	4 636	0 197		2 76	0 202
	6 415	0 181		6 08	0 153
	8 136	0 162		6 66	0 142
HI	0 800	0 240		6 91	0 140
	1 430	0 217		8 72	0 110

have a minimum in it. With the exception of potassium and rubidium sulfates, most sulfates do show a minimum solubility at some temperature.

For the present, we offer no explanation of the fact that calcium hydroxide shows a decreasing solubility with rising temperature.

The data in the literature on the solubility of gases in aqueous salt solutions are incomplete for most gases, but sulfur dioxide will serve as an example. The solubility is given in table 4 in terms of the Bunsen absorption coefficient, which is the volume of gas at 0°C. and 760 mm. that is dissolved in one volume of water when the partial pressure of the gas is 760 mm. The temperature is 25°C. and the salt concentration is 0.5 molar.

We see here the clearly defined series: SO_4^{--}, NO_3^-, Cl^-, Br^-, SCN^-, I^-, sulfate ion decreasing and iodide ion increasing the solubility of the gas. With regard to the water equilibrium we can see that an increased solubility will result if the gas and the salt tend to shift the equilibrium in the same

direction, whereas the gas will be less soluble in water if the effects of the gas and the salt are opposed. It is not claimed that the displacement of the water equilibrium is the sole factor determining the change of solubility of a gas on adding salt. The solubility or insolubility of the salt in the liquefied gas and the solubility or insolubility of the gas in the liquefied salt are very real factors which are not being discussed in this article.

Since potassium iodide depolymerizes water and increases the solubility of sulfur dioxide, we conclude that sulfur dioxide depolymerizes water to some extent, provided we are justified in ignoring all the other factors. Since potassium sulfate increases the polymerization of water, we should expect it to decrease the solubility of the gas in water and this actually happens. For the other gases the agreement is fairly good, although the solubility in nitrate solutions seems out of line occasionally.

Bancroft and Butler (2) have shown that the solubility of succinic acid in binary mixtures of methyl, ethyl, and propyl alcohols is very nearly a

TABLE 4

Solubility of sulfur dioxide in salt solutions at 25°C.

SOLVENT	COEFFICIENT	SOLVENT	COEFFICIENT
Water	32 76	K_2SO_4	30 42
Na_2SO_4	29 28	KNO_3	30 97
NaCl	29 74	KCl	31 53
NaBr	30 93	KBr	32 97
NaSCN	32 47	KSCN	34 42
		KI	35 42

straight line function of the composition of the alcohol mixture. This shows that any change in polymerization of the alcohols has little or no effect. In mixtures of water with any one of these alcohols there is a maximum solubility, which cannot be due entirely to compound formation, because the position of the maximum is displaced sideways with changing temperature. Assuming that the effect of the alcohol is additive, it is possible to calculate the apparent solvent action of water in any mixture. It was found that the water was more effective in dilute solutions. From this it seems to follow that succinic acid is much more soluble in depolymerized water than in polymerized water. The only objection to this is that, if so, the rise of boiling point for succinic acid solutions should be abnormally large, just as it is for potassium iodide solutions. This proved not to be the case and no explanation of this discrepancy is forthcoming at present.

In recent papers Barnes (4) describes experiments designed to measure the physiological effect of trihydrol in water. By freezing and melting, a water was obtained which increased the rate of growth and multiplication

of spirogyra to nine times the value observed in distilled water. The explanation offered is a displacement of the water equilibrium, with trihydrol promoting growth. We should of course like to believe this, but the evidence is unsatisfactory as yet. If this explanation is true, it means that equilibrium is reached slowly, in which case water would be a substance with a variable freezing point like acetaldoxime and benzaldoxime. Until Barnes can show that this happens, his conclusion should not be accepted by chemists. A possible explanation would be an increase in the relative amount of "heavy water." That might have a physiological effect, but in previous experiments the "heavy water" has been unfavorable to growth. An unsuspected impurity in the melted ice or in the distilled water is the most probable explanation.

Urban (25) has shown that the Hofmeister series holds for the variation of the heat capacity of water caused by the ions in a solution. All salts lower the heat capacity compared with the value for pure water. Iodides lower it least and tartrates most. Urban implies that the heat capacity will be lowered if a salt depolymerizes water, and he therefore concludes that tartrates depolymerize water the most and iodides the least, which is the reverse of what we postulate. A possible flaw in Urban's reasoning is his assumption as to the relative heat capacities of polymerized and depolymerized water. If a salt increases the relative concentration of trihydrol and if trihydrol has a lower specific heat than dihydrol, we might expect polymerization to lead to a lowering of the specific heat.

Sutherland (21) was bold enough to calculate the specific heats of trihydrol and dihydrol. While his method is not perfect, the best guess that he could make for the specific heats at 0°C. was 0.6 calorie for trihydrol and 0.8 calorie for dihydrol. Therefore polymerization does lead to a lower specific heat than depolymerization, and iodides depolymerize water more than tartrates do.

It is worth noting that Urban places the thiocyanate ion between the bromide ion and the iodide ion, just as our boiling point experiments do.

In a paper on the heats of neutralization of strong acids by strong bases, Richards and Rowe (20) point out that hydrobromic acid gives a higher heat of neutralization than hydriodic acid with lithium, sodium, or potassium hydroxide. Some data are given in table 5. The difference between hydrobromic acid and hydriodic acid with potassium hydroxide is 70 calories as against an experimental error of only 10 calories, so the difference is a real one. With sodium hydroxide the order of acids in decreasing heats of neutralization is hydrochloric, hydrobromic, nitric, and hydriodic. With potassium hydroxide the order is nitric, hydrochloric, hydrobromic, and hydriodic acid. The results are consistent for chlorides, bromides, and iodides. We do not know why sodium nitrate is out of line.

Everyone agrees that the polymerization of water increases with falling

temperature and that the reaction is therefore exothermal. The formation of water from hydrogen and hydroxyl ions is also exothermal. We can predict therefore that neutralization accompanied by polymerization will give an apparently high heat of neutralization, while the heat of neutralization will be smaller the less the polymerization. Thus we see that hydriodic acid should have a smaller heat of neutralization than hydrobromic acid, and hydrobromic acid a smaller one than hydrochloric acid, which is what Richards and Rowe found.

Another occurrence of the Hofmeister series for true solutions is the quenching of the fluorescence of various dyes by addition of salts. Jette and West (12) found that the fluorescence of aqueous solutions of quinine bisulfate, the sodium salt of fluorescein, and uranyl sulfate is extinguished by anions in the order: I^-, SCN^-, Br^-, Cl^-, NO_3^-, the iodide ion being the most effective and the nitrate the least. They say that "the order in which ions suppress the fluorescence of the substances discussed in this report is

TABLE 5

Heats of neutralization at 20°C.

$HX \cdot 100H_2O + MOH \cdot 100H_2O \rightarrow MX \cdot 201H_2O$

	KOH	NaOH	DIFFERENCE
HNO_3	14086	13837	249
HCl	14014	13895	119
HBr	13988	13843	145
HI	13915	13780	135

very similar to the well-known lyotropic series of ions [Hofmeister series] which appear in many diverse fields of physical chemistry. . . . The parallelism between the lyotropic series as usually found and that observed in fluorescence is, however, not exact. Thiocyanate in the lyotropic series usually comes beyond iodide, while we have consistently found its effect on fluorescence to be between that of bromide and iodide; and nitrate, which occurs in the lyotropic series between bromide and iodide, is in ours at the opposite end of the series from iodide. As we shall indicate, we believe these differences to be significant.

"In 1913 Heydweiller (10) pointed out that the order of the optical dispersions of negative ions for visible light was parallel to that of their precipitating power in colloid chemistry, *except that thiocyanate, instead of being beyond iodide, was intermediate between bromide and iodide.*"

Since thiocyanate ion belongs properly between bromide and iodide, and since it only comes beyond iodide when there is abnormal absorption, the objection raised by Jette and West is not sound. It seems to us that the quenching of the fluorescence may be due to the shift in the water

equilibrium produced by the ions. On this basis it would seem either that trihydrol was necessary for fluorescence in aqueous solution or that monohydrol acts against fluorescence. Iodide should therefore be most effective in extinguishing fluorescence, as it actually is. On the other hand, ethyl alcohol increases the trihydrol concentration, as is shown by the fact that in dilute solutions ethyl alcohol raises the temperature of maximum density of water (15) and therefore increases fluorescence.

This can be shown so as to prove two points. A moderately concentrated solution of fluorescein does not fluoresce, and some physicists have postulated that the high concentration of ions changed the absorption of the solution so that the fluorescent light is absorbed. No independent proof was ever given for this. If one takes a sufficiently concentrated solution of fluorescein and dilutes one half with a suitable volume of water and the other half with an equal volume of alcohol, the alcohol solution will fluoresce and the water solution will not. The concentration of ions has nothing necessarily to do with the phenomenon. The fluorescein concentration was 0.108 N in both cases and the alcohol concentration was 7 per cent.

West and Jette ascribe the occurrence of the Hofmeister series to the deformability of the ions; Banow (3) attributes it to hydration of ions; Perrin (17) accounts for the quenching of fluorescence on the basis of "collisions of the second kind"; while Büchner, Voet, and Bruins (6) believe that the Hofmeister series is related in some way to the ionic radius.

Tammann and Diekmann (23) consider that the effect of neutral salts on the electromotive force of the hydrogen electrode is due to a change in the chemical potential of the hydrogen ion and to a change in the internal pressure of the liquid. They show that a change in the salt concentration produces a change in the internal pressure.

These different explanations are incomplete but not necessarily incompatible. Tammann is ascribing the neutral salt effect in great part to a change in the solvent. A displacement of the water equilibrium would necessarily change the internal pressure. Of course it is not claimed that the change in internal pressure is due exclusively to a displacement of the water equilibrium. What is assumed to be the deformability of the ions or a hydration of the ions may perfectly well be in whole or in part a false interpretation of the phenomena accompanying the displacement of the water equilibrium. "Collisions of the second kind" is merely a phrase.

There is a great deal of work to be done in correlating the change of different properties with the displacement of the water equilibrium. For instance, Tammann and Rabe (24) show that, for the change of viscosity of salt solutions with the pressure, we get the order: nitrate, chloride, bromide, and iodide, the nitrate solution having the highest viscosity and the iodide the least. This apparently means that depolymerized water

has a lower viscosity than polymerized water. This is in accord with the behavior of pure water. At 0°C. pressures up to about 1000 kg. per square centimeter cause a decrease in the viscosity, because the displacement to the form having the smaller volume and the lower viscosity overbalances the normal increase in viscosity due to the increased pressure. At higher pressures the second factor predominates and the pressure–viscosity curve shows a minimum. At 75°C. the displacement of the water equilibrium is relatively so unimportant that no minimum shows on the curve as reproduced by Tammann and Rabe.

SUMMARY

1. The Hofmeister series holds in one form or another both for true solutions and for colloidal solutions. It must be dependent at least in part on changes in the solvent.

2. When adsorption can be excluded, the order of anions is usually sulfate, nitrate, chloride, bromide, thiocyanate, and iodide.

3. When selective adsorption comes in, the order of the anions may change. It is usual for thiocyanate and iodide to be transposed, while nitrate very often comes between chloride and bromide, and occasionally between bromide and iodide.

4. The two factors determining the Hofmeister series are the displacement of the water equilibrium and selective adsorption.

5. With gelatin the order of the anions is the same on both sides of the isoelectric point, and consequently displacement of the water equilibrium is the major factor and selective adsorption the minor factor.

6. With albumin the order of the anions reverses as the system passes from one side to the other of the isoelectric point. Consequently, displacement of the water equilibrium is the minor factor and selective adsorption the major factor.

7. The order of boiling points for equimolal solutions is sodium nitrate, sodium chloride, sodium bromide, sodium thiocyanate, and sodium iodide, the iodide solutions having the highest boiling points.

8. The order of boiling points cannot be due primarily to hydrated or hydrous ions, because the boiling point curves are more abnormal than the corresponding freezing points. Also, if we assume that the iodides are more hydrated or hydrous than the chlorides, they should peptize gelatin less readily, whereas the reverse is the case.

9. The following arbitrary assumptions have been made in order to account for the behavior of certain anions.

a. Under ordinary conditions liquid water may be considered as essentially a mixture of trihydrol, dihydrol, and monohydrol coëxisting in reversible equilibrium.

b. Chloride, bromide, thiocyanate, and iodide ions tend to change dihy-

drol into monohydrol and have no especial effect on trihydrol beyond that which is a necessary consequence of the displacement of the equilibrium between dihydrol and monohydrol. The order of increasing effectiveness is chloride, bromide, thiocyanate, and iodide.

c. The nitrate ion tends to convert trihydrol into monohydrol. For equivalent concentrations the amount of monohydrol is less with nitrate ion than with chloride ion.

d. The sulfate ion tends to convert trihydrol and monohydrol into dihydrol.

e. The electrolytic solution pressure of hydrogen is greater in dihydrol than in monohydrol, and that of oxygen is less.

10. The order of anions in lowering the temperature of maximum density of water is chloride, bromide, iodide, nitrate, and sulfate, the sulfate being the most effective.

11. Alcohol raises the temperature of maximum density of water and therefore increases the trihydrol concentration.

12. Working in 80 to 95 per cent alcohol it was possible to show that thiocyanate is adsorbed more strongly by gelatin than iodide and nitrate than chloride.

13. The neutral salt effect occurs both with strong and with weak acids when sodium chloride or sodium bromide is used as the neutral salt. The dissociation constant of carbonic acid has been increased one thousandfold and this is not the limiting value.

14. The single potential difference $H_2 \mid HCl$ is greater than that for $H_2 \mid HBr$ when the two acids are equimolal.

15. The decreasing solubility of anhydrous sodium sulfate with rising temperature is due to displacement of the water equilibrium.

16. On adding salts to a solution of sulfur dioxide in water, the solubility changes in the order: SO_4^{--}, NO_3^-, Cl^-, Br^-, SCN^-, and I^-, sulfate ion causing a decrease in solubility and iodide ion an increase. From this we deduce that sulfur dioxide tends to depolymerize water.

17. Succinic and adipic acids are apparently more soluble in depolymerized water than in polymerized water, but the boiling point curve for succinic acid in water is not as abnormal as it should be and some factor may have been overlooked.

18. There is no satisfactory evidence as yet to show that spirogyra grows more rapidly in polymerized than in depolymerized water.

19. The heat capacities of salt solutions and the heats of neutralization vary from chloride to bromide as they should, but the heat of neutralization of sodium hydroxide by nitric acid is apparently out of line.

20. The fluorescence of aqueous solutions of quinine bisulfate, the sodium salt of fluorescein, and uranyl sulfate can be extinguished by addition of salts. The order of decreasing effectiveness of the anions is: I^-, SCN^-, Br^-, Cl^-, and NO_3^-.

21. A concentrated solution of fluorescein does not fluoresce. This is not due to an electrostatic effect changing the absorption, because it is possible to dilute to a certain extent with water without bringing back the fluorescence, while diluting with the same volume of alcohol causes fluorescence. That seems to indicate that trihydrol promotes fluorescence and monohydrol checks it.

22. The displacement of the water equilibrium changes the internal pressure, iodide raising it more than chloride.

23. The phenomena now ascribed to deformability of ions and to hydration of ions can probably be better ascribed, at least in part, to displacement of the water equilibrium.

24. The changes in viscosity of water and of salt solutions with changing pressure fit in very well under the concept of displacement of the water equilibrium by pressure and by salts.

25. Since the Debye-Hückel theory postulates interaction of the ions as the only disturbing factor, this theory must break down for all concentrations at which the displacement of the water equilibrium is a disturbing factor.

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ELECTROKINETIC PROPERTIES OF PROTEINS. II

Adsorption of Gliadin at Glass–Liquid Interface as Influenced by Hydrogen-ion Concentration[1,2]

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In the streaming potential studies reported in an earlier paper (11), the isoelectric points of some of the wheat proteins were interpolated from the values for the ζ-potential of the protein–liquid interface. The latter were calculated from the streaming potential data by the formula for diaphragms developed by Briggs (2)

$$\zeta = \frac{4\pi\eta\kappa_s H}{P\epsilon} \tag{1}$$

in which η is the viscosity of the liquid, κ_s the electrical conductance across the diaphragm, H the streaming potential, P the hydrostatic pressure, and ϵ the dielectric constant of the liquid.

At the isoelectric point the value for ζ is zero, and since the properties of the liquid represented by η, κ_s, and ϵ, and the hydrostatic pressure P have definite values, the streaming potential H is also equal to zero. The isoelectric point is thus the hydrogen-ion concentration at which no electromotive force is produced by streaming the solution through a diaphragm on which the protein is adsorbed.

Inasmuch as it was desired to use the isoelectric point as a differentiating property in the study of proteins, an attempt was made in this investigation to devise a convenient and rapid method for determining the electroneutral point of a protein by adsorbing it on a fritted glass diaphragm and then varying the hydrogen-ion concentration of the solution until its streaming potential fell to zero.

Preliminary experiments showed, however, that the hydrogen-ion concentration of the solution could not be experimentally adjusted to maintain the streaming potential at zero, but that a positive potential was gradually

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[2] Paper No. 29, Journal Series, from Montana State College, Agricultural Experiment Station, Bozeman, Montana.

developed. It was evident from these experiments that either the adsorption equilibrium, or the chemical equilibrium, of the proteins was disturbed by changes in the hydrogen-ion concentration of the streaming solutions. The adsorption equilibrium would, obviously, be influenced by the magnitude and sign of the charge of the protein micelles in relation to that of the adsorbent (glass particles in diaphragm), and in consequence this phase of the problem has been studied in the present work.

EXPERIMENTAL

Preparation of gliadin

Two kilograms of patent flour, from which the fatty materials had been removed by extraction with anhydrous diethyl ether, was made into a pliable dough and allowed to stand under water for 1 hour. The starch was then washed from the gluten by kneading in a stream of tap water. It was then finely divided and added to sufficient pure ethyl alcohol to form a solution containing 60 per cent of alcohol and 40 per cent of water by volume. The mixture was then placed in a mechanical shaker for 10 hours, after which it was centrifuged, filtered, and the filtrate reduced to a sirupy consistency by evaporating under reduced pressure. The gliadin was precipitated by pouring the cooled sol into a 1 per cent sodium chloride solution at 0°C., filtered, and thoroughly washed with distilled water. The precipitate was redissolved in a 60 per cent alcohol solution, its volume reduced by evaporating under reduced pressure, and again precipitated by pouring into cold 1 per cent sodium chloride solution. The re-solution and reprecipitation was repeated four times, the final precipitation being accomplished by pouring the concentrated sol into a mixture of 1 part of absolute alcohol and 1 part of anhydrous diethyl ether, after which the precipitate was washed with anhydrous ether and dried in a vacuum oven at 80°C.

Streaming potential measurements

The apparatus shown diagrammatically in figures 1 and 2 was designed to measure, by the streaming potential method, the progressive change in the potential across a solid–liquid interface when proteins, acids, alkalis, or other reagents were added to the liquid phase. Inasmuch as slight traces of electrolytes, or surface-active substances dissolved in the liquid or adsorbed at the solid–liquid interface, were readily detected by a marked change in the streaming potential, it was necessary to eliminate every possible source of contamination. Atmospheric gases such as carbon dioxide, ammonia and acid fumes were excluded from the apparatus by a counter-current of air which had been purified by bubbling successively through sulfuric acid, sodium hydroxide, and distilled water. All parts of

the apparatus coming in contact with the liquid were cleaned with hot chromic acid and rinsed with conductivity water.

The streaming cell 2 shown in figures 1 and 2 consists of a fritted glass filter crucible (Jena Glass Works No. 1bG4) with sheet platinum electrodes 1 cm. square on each side of the diaphragm. The crucible is attached at the top to an outlet receptacle bearing the upper electrode and closed at the bottom with a two-hole rubber stopper carrying the inlet tube and lower electrode.

The liquid in reservoir 1, the hydrogen-ion concentration of which is adjusted experimentally by adding acid or alkali from burettes 11 and 12,

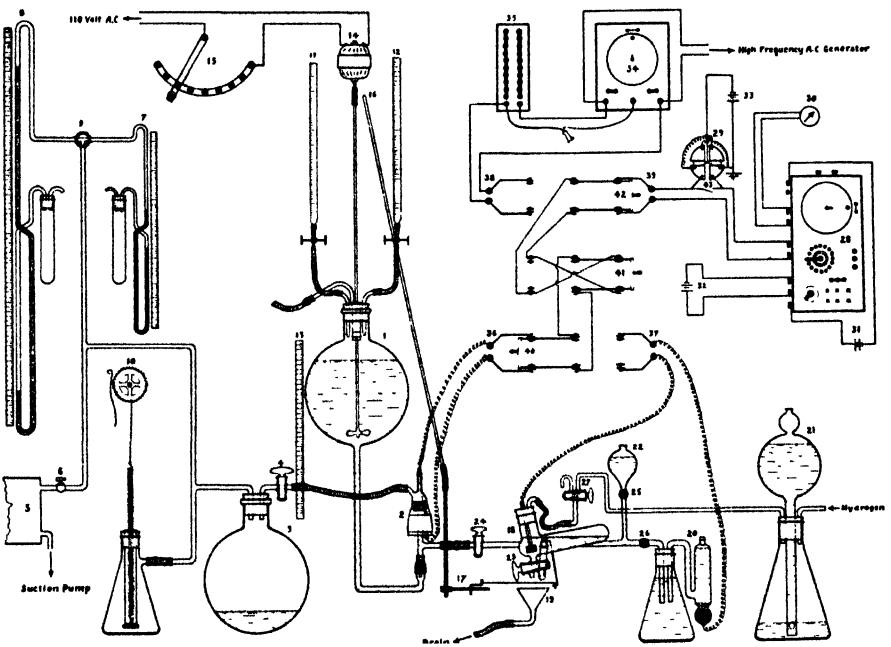

FIG. 1. STREAMING POTENTIAL APPARATUS

is streamed through the diaphragm of cell 2 into flask 3 by suction. The air in flask 3 is exhausted through needle valve 6 into tank 5 which is evacuated by a water pump. The hydrostatic pressure under which the liquid streams through the diaphragm may be measured by either the mercury manometer 7 or the water manometer 8, or both, by adjusting the three-way stopcock 9, the pressure being maintained constant by the automatic regulator 10. Stopcock 4 is closed when it is desired to stop the streaming liquid without readjusting the hydrostatic pressure.

The electromotive force produced by streaming the liquid through the fritted glass diaphragm in cell 2 is measured by connecting the electrodes in cir-

cuit with the potentiometer (28) and Compton electrometer (29). Switches 40 and 42 are set in contact with 36 and 39, respectively, and the reversing switch 41 is set so that the positive electrode of the streaming cell is connected to the positive binding post of the potentiometer. The electromotive force supplied to the potentiometer by the 2-volt lead storage cell (31) is balanced against that of the standard cadmium cell (32), the null-point being indicated by the galvanometer (30). The electrometer, which is used to indicate the null-point in balancing the electromotive force from the potentiometer against the streaming potential, is operated on a charge of 90 volts by connecting two radio "B" batteries (33) in series between the needle and one pair of quadrants.

After adjusting the electrometer to its zero-point, switch 43 connecting the two pairs of quadrants is opened and the liquid caused to stream

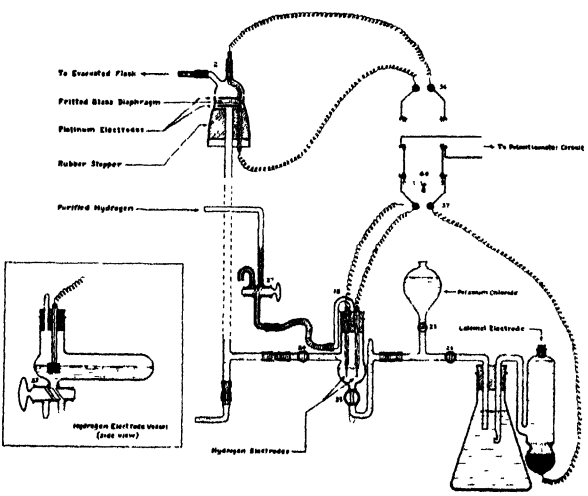

FIG. 2. STREAMING-CELL AND HYDROGEN ELECTRODE APPARATUS

through the diaphragm by opening needle valve 6. The hydrostatic pressure gradually increases to that automatically maintained by regulator 10, while at the same time the increasing potential across the diaphragm is balanced by adjusting the potentiometer experimentally. The applied hydrostatic pressure may be increased or decreased by changing the tension of the helical spring of the pressure regulator, after which it remains constant during the progress of the experiment. The effective hydrostatic pressure decreases slightly, however, owing to the lowering of the liquid in reservoir 1. This difference in level between the liquid in 1 and the end of the discharge tube in 3 is read directly from scale 13 in millimeters, divided by 13.6, and added to the pressure indicated by the manometers.

If the diaphragm or the streaming liquid have not been contaminated in any way, the system will come to equilibrium in one or two minutes, and

the streaming potential will remain constant except for a slight gradual decrease due to the lowering of the level of the liquid in the reservoir.

The system being in equilibrium and the streaming potential constant, except for the slight change explained above, a measured volume of standard gliadin solution containing 0.002 g. of gliadin for each liter of streaming liquid is added and the solution quickly homogenized by the mechanical stirrer 14, the speed of which is regulated by rheostat 15. The time of adding the gliadin is recorded and the change in streaming potential measured at 2-minute intervals for 10 minutes, and at 5-minute intervals thereafter.

Electrical resistance across diaphragm

With the liquid still flowing, switch 43 is closed and the streaming cell thrown in circuit with the conductivity apparatus by setting switches 40 and 42 in contact with 36 and 38, respectively. The resistance across the diaphragm is then balanced against the adjustable resistances 35 by means of the Kohlrausch slide wire 34, a pair of ear-phones being used to detect the null-point. With solutions of high resistance in the streaming cell, the slide wire could not be accurately balanced by the telephone detector, and in consequence three or more determinations were made and the average of these used in the calculations. Bull and Gortner (6) overcame this difficulty by using an alternating current galvanometer instead of the telephone detector.

After completing the streaming potential, hydrogen-ion concentration, and electrical resistance measurements, the cell constant was determined by replacing the liquid in the cell with a standard solution (10) composed of 0.7476 g. of potassium chloride and 1000 g. of redistilled water. The resistance of the cell was measured with the standard solution streaming through the diaphragm under the same hydrostatic pressure used in making streaming potential measurements.

Hydrogen-ion concentration of streaming liquid

Although the glass electrode might have been used advantageously in determining the hydrogen-ion concentration of the extremely dilute unbuffered solutions, it has not, perhaps, been investigated sufficiently to justify its use as a routine method. The better known hydrogen electrode was therefore used in the apparatus shown in figures 1 and 2.

The hydrogen electrode vessel (18) is filled by closing stopcock 23, opening 24 and 27 and tilting it so that it is filled with the liquid, thereby displacing the air upward and out through stopcock 27. Stopcock 24 is then closed, 23 opened and the vessel tilted down, after which 27 is turned to permit hydrogen gas to displace the liquid from the vessel into drain 19. These operations are repeated several times to free the system from oxygen.

All stopcocks are finally closed with the vessel about one-quarter filled with liquid. Stopcock 27 is then turned so that the hydrogen pressure from reservoir 21, which is equal to about 15 cm. of water above that of the atmosphere, is maintained within the hydrogen electrode vessel. This not only saturates the platinum electrodes more quickly, but prevents the atmospheric gases from diffusing into the system. It also causes the films of liquid in the ground glass joints of stopcocks 23 and 24 to move outward instead of inward, thus reducing error from this source.

The vessel is then gently shaken by the geared mechanism 17 by connecting shaft 16 to the motor 14 with a short piece of rubber tubing, the speed of the motor being regulated by the rheostat 15. The system is saturated with hydrogen within four minutes, after which the motor is stopped with the liquid in the electrode end of the vessel. With the system still under pressure from the hydrogen reservoir, stopcock 23 is turned to discharge from the bore of the stopcock plug, and from the tube between the stopcock and the vessel, the solution which has not been saturated with hydrogen. The pressure within the vessel is then released through 27, after which 23 is carefully turned to connect the vessel with the calomel electrode 20. Stopcock 25 is then carefully opened and saturated potassium chloride solution flows from reservoir 22 and rises slowly in the tube above the stopcock, forming a well defined and easily reproducible liquid junction. When the liquid junction has risen to a mark on the tube midway between stopcock 23 and the vessel, 27 is closed to prevent the potassium chloride from rising too high and mixing with the liquid. The plug in 26 is greased only at the ends to facilitate electrical conductance when the stopcock is closed. The difference in potential between the hydrogen and the calomel electrodes is measured by throwing switches 40 and 42 in contact with 37 and 39, respectively. The electromotive force is then balanced with the potentiometer, using the quadrant electrometer as a null-point instrument. The potential of each of the twin hydrogen electrodes is measured and two complete determinations made on each solution.

Calculation of the electric moment of the double layer

From the streaming potential data may be calculated either the ζ-potential or the electric moment of the double layer. For the reasons set forth by Bull and Gortner (7) the electric moment is preferable, and accordingly the data obtained in the present work have been computed to this basis. The formula for the electric moment given by Bull and Gortner is

$$qd = \frac{\eta \kappa_s H}{P} = \mu \tag{2}$$

where q is the charge per unit area of the double layer in electrostatic units, d the thickness of the double layer in centimeters, η the viscosity of the

streaming liquid in poises, κ_s the electrical conductance across the diaphragm in reciprocal ohms, H the streaming potential in volts, and P the hydrostatic pressure in centimeters of mercury. The product qd (charge $\times$ distance) is the electric moment per square centimeter of the double layer and is represented by μ. Remembering, however, that one C.G.S. electrostatic unit of potential is equal to 299.86 absolute volts, and that the C.G.S. electrostatic unit of conductance is equal to 1.112151×10^{-12} ohm^{-1} cm.^{-1} (9); and that the density of mercury is 13.6, and the force of gravity 981 dynes, the different quantities in the above equation are converted to C.G.S. units by evaluating the constants to give the simplified expression:

$$\mu = 224755.22 \times \eta \times \frac{\kappa_s H}{P} \tag{3}$$

For convenience in comparing the data presented in this paper with the more familiar ζ-potential in the literature, the relation of the two may be expressed by substituting the ζ-potential formula developed by Briggs (2).

$$\zeta = 847{,}649{,}450 \times \frac{\eta}{\epsilon} \times \frac{\kappa_s H}{P} \tag{4}$$

in equation 3, which gives

$$\zeta = \frac{3771.43\ \mu}{} \tag{5}$$

or

$$\mu = 2.65 \times 10^{-4} \times \epsilon\zeta \tag{6}$$

where ϵ is the value for the dielectric constant used in the original calculations. Although the value for ϵ generally used in calculating the ζ-potential from streaming potential data is probably incorrect, as explained by Bull and Gortner (7), expressions 5 and 6 may be used to convert the data of this and other papers to a comparable basis.

DISCUSSION

Fritted glass discs on filter crucibles are satisfactory diaphragms for streaming potential measurements, because they are composed of glass particles of uniform size and are of sufficient porosity to produce results not in error due to "back-pressure" effects. The importance of uniformity of size of particles in streaming potential diaphragms has been emphasized by Bull and Gortner (6), whose experiments showed that the streaming potential was a linear function of hydrostatic pressure only when the particles in the diaphragms were homogeneous in size. The effect of size of pores on the streaming potential has also been investigated by Bull (4),

whose experimental data showed that an appreciable "back-pressure" was developed by electroösmotic flow if the radius of the capillaries was 1 μ or smaller.

The data in table 1 and the graphs in figures 3 and 4 show that the glass diaphragms were negatively charged in both acidic and basic solutions. The magnitude of the charge, however, was a function of the total ionic concentration rather than of the concentration of hydrogen ions. This is shown by the relation of the values for the electric moment to those for the specific electrical conductivity of the solution, a relationship similar to that observed by Bull and Gortner (5) for cellulose in aqueous solutions of inorganic salts.

TABLE 1

Electric moment of the double layer at the solid–liquid interface of a fritted glass diaphragm as influenced by hydrogen-ion concentration

STREAMING LIQUID	pH	$\kappa_s \times 10^{-6}$	η	TEMPERATURE	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
		ohms^{-1}	*poises*	*degrees C*	*mm Hg*	*millivolts*	*e.s.u.* $\times 10^{-4}$
HCl	5 69	1 76	0 0089	25 2	124	−1230	−3 49
HCl	5.22	3 02	0 0084	27 9	124	−874	−4 02
HCl	4 82	5 96	0 0085	27 4	125	−643	−5 86
HCl	4.43	12 62	0 0087	26 2	124	−386	−7 69
HCl	4.25	17 48	0 0087	26 1	125	−320	−8 75
HCl	3 20	36 43	0 0093	23 5	125	−257	−15 67
NaOH	7.76	2 42	0 0088	25 0	125	−1315	−5 04
NaOH	8 16	3.82	0 0086	26 9	125	−1134	−6.70
NaOH	9.06	10 22	0.0084	27 7	126	−724	−11.10
NaOH	9 44	17 68	0 0084	27 8	124	−524	−14 12
NaOH	9.65	23.71	0 0087	26 4	123	−434	−16 37
NaOH	9.74	43 81	0 0089	25 3	124	−237	−16 76
NaOH	9.94	48 19	0 0085	27 1	125	−244	−17.99

The results of the adsorption studies given in table 2 and presented graphically in figures 5 and 6 show that the electrostatic charge of the double layer at the glass–liquid interface is reversed upon adding protein to the streaming liquid if its hydrogen-ion concentration is on the acid side of the isoelectric point of the protein. The negatively charged glass surface apparently adsorbs a layer of positively charged protein and assumes its electrokinetic properties. The behavior of the glass is thus similar to that of quartz particles used by Briggs (3), Freundlich and Abramson (8), and by Svedberg and Tiselius (12). Recently Abramson (1) has shown that the isoelectric point, the cataphoretic mobility, and the dissociation constant of serum albumin and egg albumin are very nearly the same when adsorbed on quartz as when dispersed in solution. The

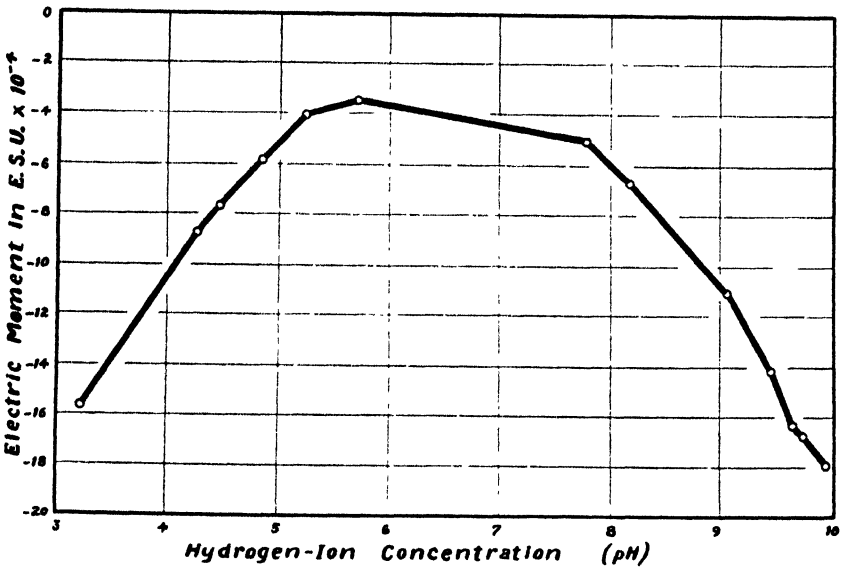

FIG. 3. ELECTRIC MOMENT OF DOUBLE LAYER AT GLASS-LIQUID INTERFACE AS INFLUENCED BY HYDROGEN-ION CONCENTRATION

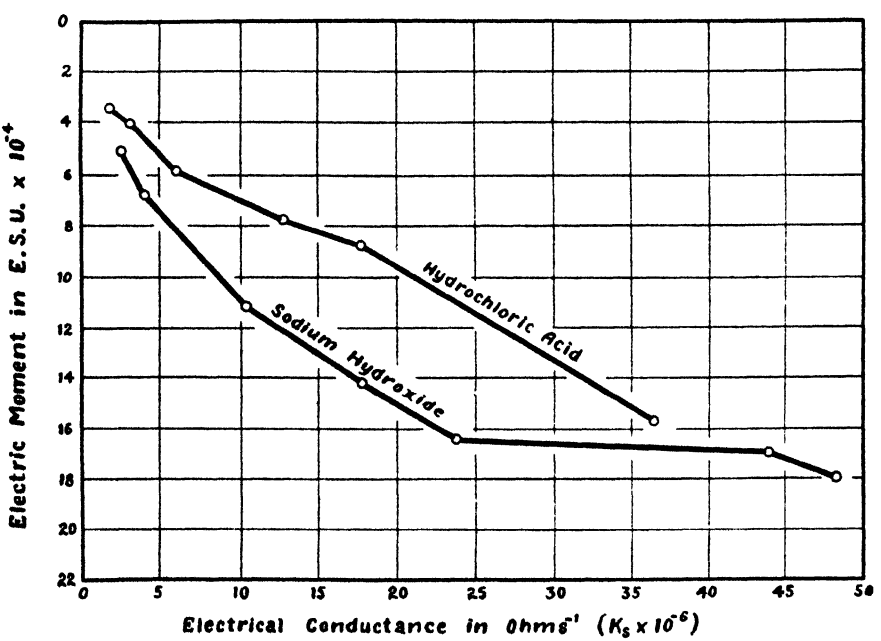

FIG. 4. ELECTRIC MOMENT OF DOUBLE LAYER AT GLASS-LIQUID INTERFACE AS INFLUENCED BY TOTAL IONIC CONCENTRATION (ELECTROLYTIC CONDUCTIVITY OF SOLUTION)

TABLE 2

Influence of hydrogen-ion concentration on the rate of adsorption of gliadin at a glass–liquid interface as indicated by change in the electric moment of the double layer

TIME	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
Distilled water; pH = 6.41; $\kappa_s = 1.59 \times 10^{-6}$; $\eta = 0.0090$; $T = 24.9°C$.			
minutes	*mm.* Hg	*mv.*	*e.s.u* $\times 10^{-4}$
0	127	−1316	−3.33
5	126	−1304	−3.33
10	125	−1297	−3.34
15	124	−1290	−3 35
20	124	−1285	−3.34
0.002 g. gliadin per liter added			
22	123	−920	−2.41
24	123	−638	−1.67
26	122	−390	−1.03
28	122	−195	−0 51
30	121	−38	−0 10
35	120	+325	+0.87
40	120	+558	+1.50
45	119	+738	+2.00
50	118	+862	+2.32
55	118	+956	+2.61
60	117	+1007	+2 77
65	116	+1053	+2 92
70	115	+1084	+3.03
75	115	+1102	+3.08
HCl solution, pH = 5.69; $\kappa_s = 1.76 \times 10^{-6}$; $\eta = 0.0089$; $T = 25.2°C$.			
0	126	−1246	−3.49
5	125	−1237	−3 49
10	124	−1231	−3.50
15	124	−1222	−3 48
20	123	−1215	−3 49
0.002 g. gliadin per liter added			
22	123	−809	−2 32
24	122	−402	−1.16
26	122	−51	−0 15
28	122	+299	+0.86
30	121	+538	+1.57
35	121	+911	+2.66
40	120	+1134	+3.33
45	119	+1269	+3.76
0.002 g. gliadin per liter added—*Cont'd*			
minutes	*mm.* Hg	*mv.*	*e.s.u.* $\times 10^{-4}$
50	118	+1355	+4.05
55	117	+1410	+4.25
60	117	+1453	+4.38
65	116	+1494	+4.54
70	115	+1517	+4.65
75	114	+1526	+4.72
80	113	+1528	+4.77
85	112	+1525	+4.80
HCl solution; pH = 5.22; $\kappa_s = 3.02 \times 10^{-6}$; $\eta = 0.0084$; $T = 27.9°C$.			
0	126	−884	−4.01
5	125	−879	−4 02
10	124	−874	−4.03
15	123	−869	−4 04
20	123	−863	−4.01
0.002 g. gliadin per liter added			
22	122	−208	−0.97
24	122	+154	+0 72
26	121	+321	+1.52
28	121	+401	+1.89
30	121	+459	+2.17
35	120	+530	+2.52
40	119	+563	+2.70
45	118	+593	+2.87
50	118	+616	+2 98
55	117	+631	+3.08
60	116	+644	+3.17
65	115	+657	+3.26
70	115	+663	+3.29
75	113	+669	+3.38
80	111	+666	+3.43
HCl solution; pH = 4.82; $\kappa_s = 5.96 \times 10^{-6}$; $\eta = 0.0085$; $T = 27.4°C$.			
0	127	−651	−5.84
5	126	−648	−5.86
10	125	−643	−5.86
15	124	−639	−5.87
20	124	−635	−5.84

TABLE 2—*Continued*

TIME	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
0.002 g. gliadin per liter added			
minutes	*mm.* Hg	*mv.*	*e.s.u.* × 10
22	123	−241	−2.23
24	123	+63	+0.58
26	122	+204	+1.90
28	122	+264	+2.47
30	121	+291	+2.74
35	121	+322	+3.03
40	120	+342	+3 25
45	119	+350	+3 35
50	118	+356	+3.44
55	117	+360	+3 51
60	117	+364	+3.55
65	116	+362	+3.56
70	115	+367	+3.64
75	114	+366	+3.66
80	113	+363	+3.66
HCl solution; pH = 4.43; κ_s = 12.62 × 10^{-6}; η = 0.0087; T = 26.2°C.			
0	126	−392	−7.68
5	125	−389	−7.68
10	124	−386	−7 69
15	124	−383	−7 63
20	123	−382	−7.67
0.002 g. gliadin per liter added			
22	123	−14	−0.28
24	123	+97	+1.95
26	122	+128	+2 59
28	122	+169	+3 42
30	122	+195	+3.95
35	121	+204	+4.16
40	121	+207	+4 22
45	120	+210	+4.32
50	119	+211	+4.38
55	119	+215	+4.46
60	118	+218	+4.56
65	117	+217	+4.58
70	117	+222	+4.69
75	116	+225	+4.79
HCl solution; pH = 4.25; κ_s = 17.48 × 10^{-6}; η = 0.0087; T = 26.1°C.			
0	127	−325	−8.76
5	126	−322	−8.74
10	125	−319	−8.73
15	124	−317	−8 75
20	123	−315	−8 76
0.002 g. gliadin per liter added			
22	123	−3	−0 08
24	122	+139	+3.90
26	122	+175	+4 91
28	122	+182	+5.10
30	121	+200	+5 66
35	121	+209	+5 91
40	120	+206	+5.87
45	120	+205	+5 85
50	119	+201	+5.78
55	118	+197	+5 71
60	118	+193	+5 60
65	117	+189	+5 53
70	116	+186	+5.49
75	115	+186	+5 53
HCl solution; pH = 3.20; κ_s = 36.43 × 10^{-6}; η = 0.0093; T = 23.5°C.			
0	127	−260	−15 61
5	126	−259	−15 67
10	125	−256	−15 61
15	125	−255	−15 55
20	124	−253	−15 55
0.002 g. gliadin per liter added			
22	124	−100	−6.15
24	123	+46	+2 85
26	123	+95	+5 89
28	122	+106	+6 62
30	122	+112	+7.00
35	121	+113	+7 12
40	120	+115	+7 30
45	120	+115	+7.30
50	119	+114	+7.30
55	118	+117	+7.56
60	118	+113	+7.30
65	117	+115	+7.49
70	117	+116	+7.56
75	116	+115	+7.56
80	115	+117	+7.75
85	114	+115	+7.69

TABLE 2—*Continued*

TIME	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
NaOH solution; pH = 7.53; κ_s = 2.84 × 10^{-6}; η = 0.0089; T = 25.2°C.			
minutes	*mm.* Hg	*mv.*	*c.s.u* × 10^{-4}
0	125	−1167	−5 27
5	125	−1158	−5 27
10	124	−1150	−5 27
15	123	−1144	−5 29
20	123	−1137	−5 26
0.002 g. gliadin per liter added			
22	122	−1264	−5 89
24	122	−1375	−6 41
26	122	−1451	−6 76
28	121	−1519	−7.14
30	121	−1560	−7 28
35	120	−1579	−7 48
40	119	−1593	−7 61
45	118	−1596	−7.69
50	118	−1590	−7.66
55	117	−1581	−7 68
60	116	−1561	−7.65
65	115	−1549	−7 66
70	114	−1538	−7 67
75	114	−1531	−7.64
NaOH solution; pH = 7.14; κ_s = 2.04 × 10^{-6}; η = 0.0089; T = 25.4°C.			
0	124	−1215	−4 00
5	123	−1207	−4 01
10	123	−1198	−3 98
15	122	−1191	−3 99
20	121	−1186	−4 00
0.002 g. gliadin per liter added			
22	121	−1239	−4.18
24	121	−1272	−4.29
26	120	−1285	−4 37
28	120	−1296	−4 41
30	120	−1302	−4 43
35	119	−1304	−4 47
40	118	−1295	−4 48
45	117	−1288	−4.50
50	117	−1281	−4.47
55	116	−1277	−4.50
60	115	−1272	−4.52
65	114	−1267	−4.54
70	113	−1255	−4.54
75	112	−1242	−4.53

TIME	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
NaOH solution; pH = 7.76; κ_s = 2.42 × 10^{-6}; η = 0.0088; T = 25.0°C.			
minutes	*mm* Hg	*mv.*	*c s u.* × 10^{-4}
0	122	−1330	−5 02
5	126	−1323	−5 04
10	125	−1316	−5.05
15	124	−1307	−5 06
20	124	−1299	−5 03
0.002 g. gliadin per liter added			
22	123	−1597	−6 23
24	122	(exceeded range of potentiometer)	
NaOH solution; pH = 8.16; κ_s = 3.82 × 10^{-6}; η = 0.0086; T = 26.9°C.			
0	126	−1138	−6 67
5	125	−1135	−6 70
10	125	−1135	−6.70
15	124	−1132	−6 74
20	124	−1130	−6 73
0.002 g. gliadin per liter added			
22	124	−1294	−7.70
24	123	−1423	−8 54
26	123	−1520	−9 12
28	123	−1555	−9.33
30	122	−1573	−9 52
35	121	−1599	−9.76
40	120	−1604	−9 87
45	119	−1598	−9.91
50	119	−1589	−9.86
55	118	−1559	−9.75
60	117	−1525	−9.62
65	117	−1511	−9.53
70	116	−1499	−9.54
75	114	−1468	−9.51
NaOH solution; pH = 9.06; κ_s = 10.22 × 10^{-6}; η = 0.0084; T = 27.7°C.			
0	127	−726	−11.04
5	127	−725	−11.02
10	126	−724	−11.10
15	126	−724	−11.10
20	125	−722	−11.15

TABLE 2—*Continued*

TIME	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
0 002 g. gliadin per liter added			
minutes	*mm* Hg	*mv*	*e s u* × 10^{-4}
22	125	−738	−11.40
24	125	−750	−11 59
26	124	−762	−11 87
28	123	−759	−11 92
30	123	−759	−11 92
35	122	−756	−11 97
40	121	−752	−12 00
45	121	−748	−11 94
50	120	−748	−12 04
55	119	−734	−11 91
60	118	−720	−11 78
65	117	−710	−11 72
70	116	−701	−11 67
75	115	−691	−11 60
80	114	−682	−11 55
NaOH solution; pH = 9.44; κ_s = 17.68 × 10^{-6}; η = 0.0084; T = 27.8°C.			
0	126	−532	−14 10
5	125	−527	−14 08
10	124	−523	−14 09
15	123	−521	−14.15
20	122	−519	−14 21
0.002 g. gliadin per liter added			
22	122	−514	−14 07
24	122	−509	−13.94
26	121	−505	−13 94
28	121	−498	−13.75
30	120	−492	−13 70
35	120	−478	−13 31
40	119	−468	−13.14
45	118	−461	−13 05
50	117	−450	−12.85
55	117	−443	−12.65
60	116	−439	−12.64
65	115	−434	−12.61
70	114	−429	−12.57
75	113	−423	−12.51
NaOH solution; pH = 9.65; κ_s = 23.71 × 10^{-6}; η = 0.0087; T = 26.4°C.			
0	124	−437	−16.35
5	124	−436	−16.32
NaOH solution; pH = 9.65; κ_s = 23.71 × 10^{-6}; η = 0.0087; T = 26.4°C.—*Cont'd*			
minutes	*mm* Hg	*mv*	*e s u* × 10^{-4}
10	123	−434	−16 37
15	123	−432	−16 30
20	122	−430	−16 35
0.002 g. gliadin per liter added			
22	122	−425	−16 16
24	122	−414	−15 74
26	121	−405	−15 53
28	121	−397	−15 22
30	120	−392	−15 16
35	120	−375	−14 50
40	119	−366	−14 27
45	118	−357	−14 04
50	117	−349	−13 84
55	116	−346	−13 84
60	116	−340	−13 60
65	115	−335	−13 52
70	114	−330	−13 43
75	112	−324	−13 42
NaOH solution; pH = 9.74; κ_s = 43.81 × 10^{-6}; η = 0.0089; T = 25.3°C.			
0	126	−241	−16.78
5	125	−239	−16 77
10	124	−237	−16.76
15	123	−235	−16 76
20	122	−233	−16 75
0.002 g. gliadin per liter added			
22	122	−210	−15.10
24	122	−198	−14 23
26	121	−182	−13 19
28	121	−174	−12 61
30	121	−167	−12.11
35	120	−159	−11 62
40	119	−152	−11 20
45	118	−144	−10 70
50	118	−140	−10 41
55	117	−140	−10 49
60	117	−138	−10.35
65	116	−135	−10.21
70	115	−131	−9.99
75	114	−131	−10.08
80	113	−129	−10.01

TABLE 2—*Concluded*

TIME	HYDROSTATIC PRESSURE	STREAMING POTENTIAL	ELECTRIC MOMENT OF DOUBLE LAYER
NaOH solution; pH = 9.94; $\kappa_s = 48.19 \times 10^{-6}$; $\eta = 0.0085$; $T = 27.1°C$.			
minutes	*mm.* Hg	*mv.*	*e.s.u.* $\times 10^{-4}$
0	127	−249	−18.07
5	126	−246	−17.99
10	125	−244	−17.99
15	124	−242	−17.98
20	123	−240	−17.98
0.002 g. gliadin per liter added			
22	122	−212	−16.01
24	122	−195	−14.73
26	122	−187	−14.12
0.002 g. gliadin per liter added.—*Cont'd*			
minutes	*mm.* Hg	*mv.*	*e.s.u.* $\times 10^{-4}$
28	121	−180	−13 71
30	121	−177	−13.48
35	120	−166	−12.75
40	119	−160	−12.39
45	118	−156	−12.18
50	118	−152	−11.87
55	117	−146	−11.50
60	116	−141	−11.20
65	115	−135	−10.82
70	114	−131	−10.59
75	113	−125	−10.19

reversal of the charge of the fritted glass diaphragm when protein was added to the streaming liquid, therefore represents the transition from a glass–liquid to a protein–liquid system; and the rate of change, as indicated by the electric moment of the double layer, is an index of the rate of adsorption of the protein.

As shown by the slopes of the curves in figure 5 for the acid solution, the rate of adsorption was most rapid for the highest hydrogen-ion concentrations and slowest for the low. The adsorption rate appears to be dependent upon the difference in the charge on the glass particles composing the diaphragm and that of the protein micelles. For example, the charge at the glass–liquid interface is -3.34×10^{-4} E.S.U. at pH 6.41 and -15.60×10^{-4} E.S.U. at pH 3.20, while that at the protein–liquid interface is $+3.08 \times 10^{-4}$ and $+7.56 \times 10^{-4}$ E.S.U., respectively, for the same two solutions. The latter two values are those for the electric moment of the double layer 55 minutes after adding the protein to the streaming liquid, or 75 minutes after beginning the experiment. Although the system had not attained equilibrium, as shown by the slope of the curves in figure 5, the above values are relative. The electrostatic charge of the protein–liquid interface with respect to that of the glass–liquid interface is thus 6.42×10^{-4} E.S.U. at pH 6.41 and 23.16×10^{-4} E.S.U. at pH 3.20. The rates of adsorption were approximately in the proportion of 23 to 6, as indicated by the slopes of the curves, that for pH 3.20 approaching as nearly to a constant value in 15 minutes as did that for pH 6.41 in 55 minutes. The other curves for the acid solution show a similar relationship.

In alkaline solutions the glass diaphragm and the protein micelles are both negatively charged, and in consequence the electrical forces of repul-

sion tend to prevent adsorption. The effect of adding proteins to the alkaline solutions on the electric moment of the double layer at the glass-liquid interface must, therefore, be attributed to changes in the composition

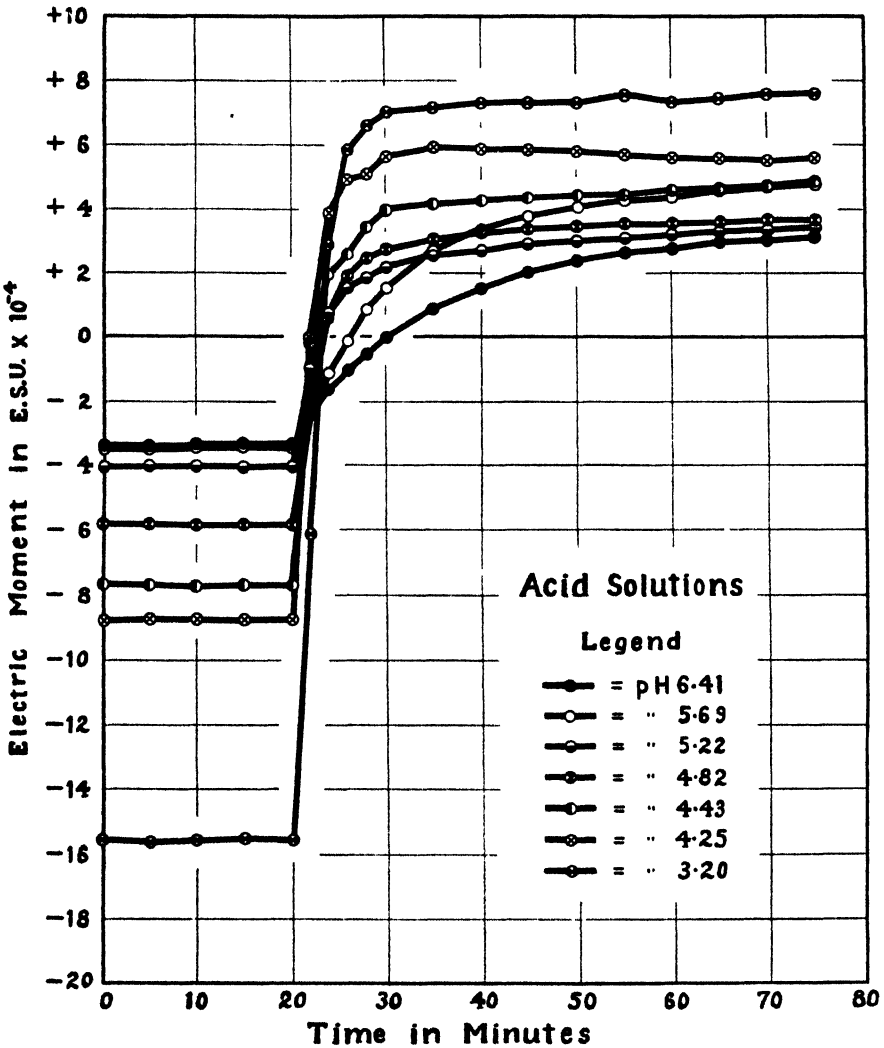

FIG. 5. RATE OF ADSORPTION OF GLIADIN AT A GLASS-LIQUID INTERFACE FROM ACIDIC SOLUTIONS AS INDICATED BY CHANGE IN THE ELECTRIC MOMENT OF THE DOUBLE LAYER

of the liquid phase due to the binding of some of the alkali by the protein. Obviously, the removal of the alkali ions from solution would reduce the total ionic concentration and increase the hydrogen-ion concentration.

As shown by the curves in figure 6 the addition of protein to solutions of pH 7.14, 7.53, 8.16, and 9.06 increased the electric moment of the double layer, whereas it decreased that in solutions more alkaline than pH 9.44,

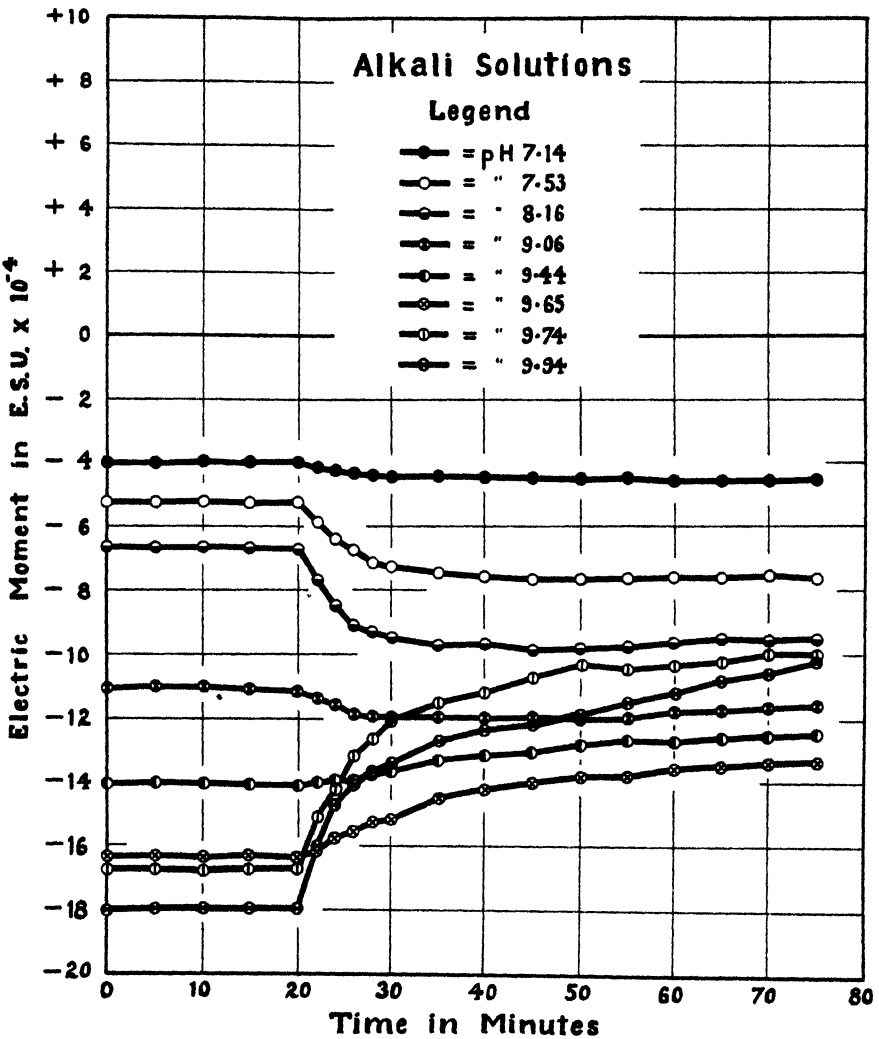

FIG. 6. RATE OF ADSORPTION OF GLIADIN AT A GLASS-LIQUID INTERFACE FROM ALKALINE SOLUTIONS AS INDICATED BY CHANGE IN THE ELECTRIC MOMENT OF THE DOUBLE LAYER

there apparently being a hydrogen-ion concentration between pH 9.04 and pH 9.44 at which no change would have occurred. That the protein was not adsorbed on the glass from alkaline solutions was also indicated by

adding increments of dilute acid to the system and observing the change in the streaming potential. At first the potential increased rapidly with successive additions of acid, then more slowly; and finally, when the isoelectric range of the protein was reached, it fell rapidly to zero and reversed in sign. The increase in the streaming potential with the addition of acid was undoubtedly due to an increase in total ionic concentration similar to that shown in figure 3, and the break and reversal of the potential in the isoelectric region apparently marked the beginning of adsorption.

SUMMARY

1. Streaming potential apparatus and methods for measuring the rate of adsorption of proteins or other substances at a glass–liquid interface are described.

2. A fritted glass diaphragm used in the streaming cell was negatively charged in both acidic and basic solutions, the magnitude of the charge being a function of the total ionic concentration rather than of concentration of hydrogen ions.

3. The rate of adsorption of gliadin at the glass–liquid interface was determined by the sign and the magnitude of the difference in the charge of the glass and of the protein micelles.

4. In the region of the isoelectric point of gliadin the adsorption equilibrium was disturbed by changes in the hydrogen-ion concentration, indicating either structural transformation of the adsorbed protein micelles, or displacement by micelles or fragments having different isoelectric points.

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THE SURFACE TENSION OF MERCURY IN A VACUUM AND IN THE PRESENCE OF HYDROGEN

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Recent determinations of the surface tension of mercury show considerable discrepancy. Popesco (11) gave a value of approximately 400 dynes per centimeter at 15°C. (corrected by Burdon (4)), Cook (6) gave 515 dynes per centimeter at 31°C., Kernaghan (8) 436.1 dynes per centimeter at 20°C., Bircumshaw (2) 480 dynes per centimeter at 20°C. The most recent value, 488 dynes, with a maximum of 491 at 25°C., observed by R. S. Burdon (4), appeared while this work was in progress. In the following paper a new modification of the flat drop method for measuring the surface tension of mercury is described. The top of the drop was located by the style of a Bourdon gauge. In addition, the variation in surface tension in the presence of hydrogen was determined. This is important in view of the recent work on activated adsorption (14). Various workers have disputed whether slow adsorption is due to the fact that only activated molecules are adsorbed, or whether solution in the bulk phase occurs through diffusion into the interior along microcapillaries. A clean mercury surface would seem, therefore, an ideal system with which to study slow adsorption, as the latter factor is absent.

THE FLAT DROP METHOD

A number of formulas have been given for deriving the surface tension σ from measurements on a flat drop. If h is the height from the top to the plane of greatest section, ρ the density, and r the radius of the above plane, then Worthington (16) found for a flat drop

$$\sigma = \tfrac{1}{2} h^2 g \rho \frac{1}{1 + 0.609\, h/r}$$

Ferguson (7 and 1) found

$$\sigma = \tfrac{1}{2} h^2 g \rho - \frac{0.609}{r} \cdot \left(\frac{g\sigma^2\rho}{2}\right)^{\frac{1}{2}}$$

For mercury these differ under the conditions below by about 0.2 per cent, and as Worthington's formula is easier to use (Ferguson's formula requires

successive approximation), and as h is uncertain to 0.05 per cent, Worthington's formula will be adopted. Porter (12) has shown that for mercury drops of radius greater than 2 cm. the above formulas agree well with the results obtained by graphical integration (Bashforth and Adams). No correction need be applied for the curvature at the top of the drop, as $\frac{h^2}{r^2}$ is only 0.01.

THE APPARATUS

The apparatus (figure 1) was made of Pyrex glass, and consists of a hemispherical cup A, 5.5 cm. in diameter, sealed into a vessel B with a window C. The cup was lipped on the inside and the edge was free from chippings.

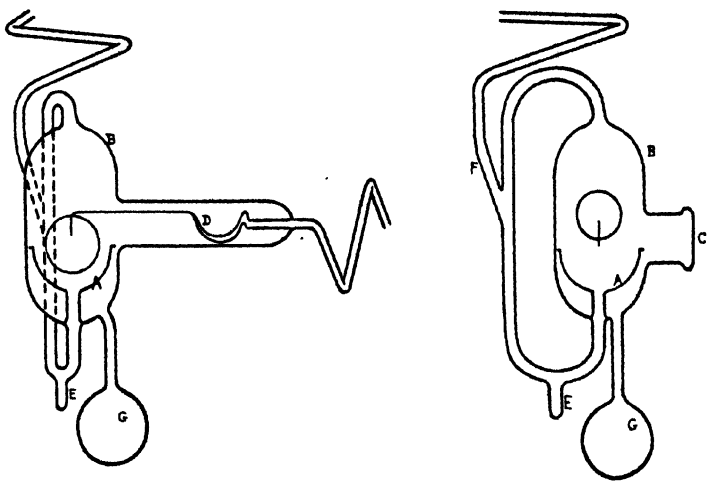

FIG. 1. DETAIL OF THE APPARATUS USED

The window was tested before it was sealed in, and no difference, to 0.001 mm., could be detected between the distance apart of two points viewed through the central portion of the window and through air. The Bourdon gauge D was arranged so that the fine tip comes just above the middle of the top surface of the cup. It would stand a pressure difference of 10 mm., and had a sensitivity of 2 mm. per millimeter change of pressure. A smooth adjustment could be made without agitating the mercury surface. Any overflow of mercury was caught in G, which could be cut off, and the mercury could easily be returned to the still. A tungsten wire could be sealed in at E. The mercury was admitted from the still at F, the spirals allowing adjustments to be made in the level of the apparatus without disconnecting.

The complete apparatus is shown in figure 2. The mercury was washed

with sodium hydroxide, air was bubbled in under a layer of dilute nitric acid and mercurous nitrate, it was distilled twice in a current of air, and then in a vacuum. It was distilled over into the cup from B. The cut-off C and the McLeod gauge were constructed so that the mercury was not fouled by rubber. There was no tap between the cut-off and the measuring apparatus, and since liquid air was always placed round the trap D when C was open, no grease vapor should have entered the apparatus; as an extra precaution a fresh sample of Apiezon grease was used in the taps, which were not exposed to strong sunlight. The Bourdon gauge could be adjusted, C being closed, by filling the space between the taps F and G with air, which was then admitted to the gauge, while the compression of the gas in the gauge by lifting the column of mercury in E gave a very fine

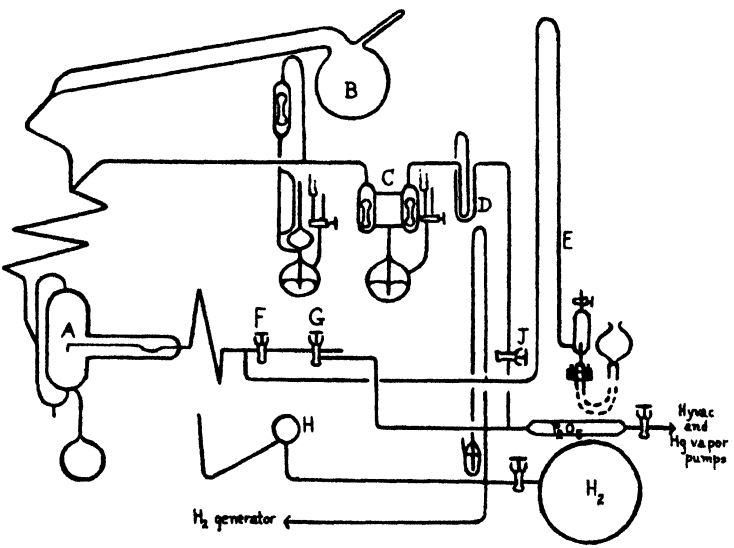

FIG. 2. THE COMPLETE APPARATUS

adjustment. To prevent the bursting of the gauge, taps F, G, J, also C were opened when gas was admitted. The tip of the style was adjusted to give an image the width of a very fine cross hair (a thin thread pulled out from rubber solution) below itself. Pressures from 1 to 15 mm. could be read on the Hamblin gauge H. With practice, readings on the mercury surface could be repeated to 0.001 mm.

The whole apparatus was washed with a solution of potassium permanganate in concentrated sulfuric acid, then with distilled water, and allowed to drain. It was joined in a moist condition, using a liquid air trap, and then pumped out and degassed by playing over it the blowpipe flame. The mercury surface was illuminated by a flash-lamp bulb, and was observed through a microscope which read to 0.001 mm. The latter was carefully

levelled and was adjusted so that the barrel racked horizontally (lycopodium powder dusted on to a flat mercury surface was observed). A flash-lamp bulb illuminated a horizontal slit which gave an image in the mercury surface at the point of largest section in the usual manner, care being taken to ensure that the slit and its image were on the same level. The room, a cellar, was constant in temperature to a degree during the winter months.

The surface tension was found to be constant over long periods of observation lasting several weeks, but for fresh distillations of mercury differed by about 1 dyne from the mean, 500.3 dynes per centimeter at 16.5°C.; this value lies between those of Burdon and Cook.

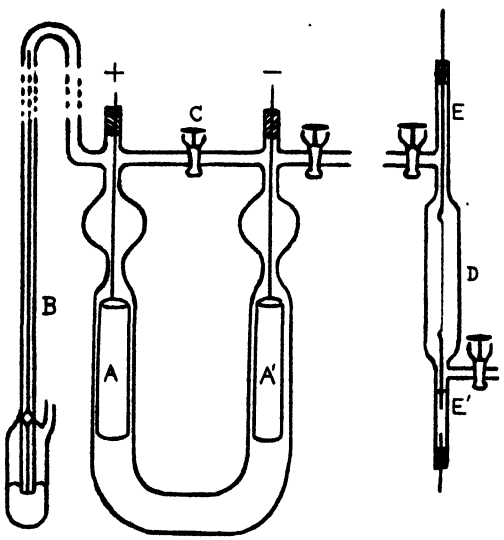

FIG. 3. APPARATUS FOR THE PREPARATION OF PURE HYDROGEN

A tungsten wire fused in at E (figure 1) was earthed, as it was thought that in the process of distillation, during which the mercury ran over glass surfaces, a charge might have been acquired. This would be dissipated only very slowly in a glass apparatus. No difference, however, was observed.

THE SURFACE TENSION OF MERCURY IN HYDROGEN

The author has experienced considerable difficulty in preparing pure hydrogen for density work, using the ordinary type of electrolytic cell. A modification was therefore devised by which the electrolyte could be thoroughly degassed before the run was made; moreover no air came in contact with it during the preparation of the gas (figure 3). The electrolyte was a solution of pure sodium hydroxide and recrystallized barium

hydroxide; the cylindrical electrodes were made from nickel sheet. The capillary tube dipped only 0.5 cm. under the surface of the mercury, so that the oxygen generated escaped at a pressure only slightly greater than atmospheric. Tap C was opened and the whole degassed with a Hyvac and mercury diffusion pump, the water finally boiling over into tubes containing sodium hydroxide. Tap C was then closed and the current passed, no difficulty being experienced in adjusting the levels of the electrolyte round A and A′, since the hydrogen comes off twice as fast as the oxygen.

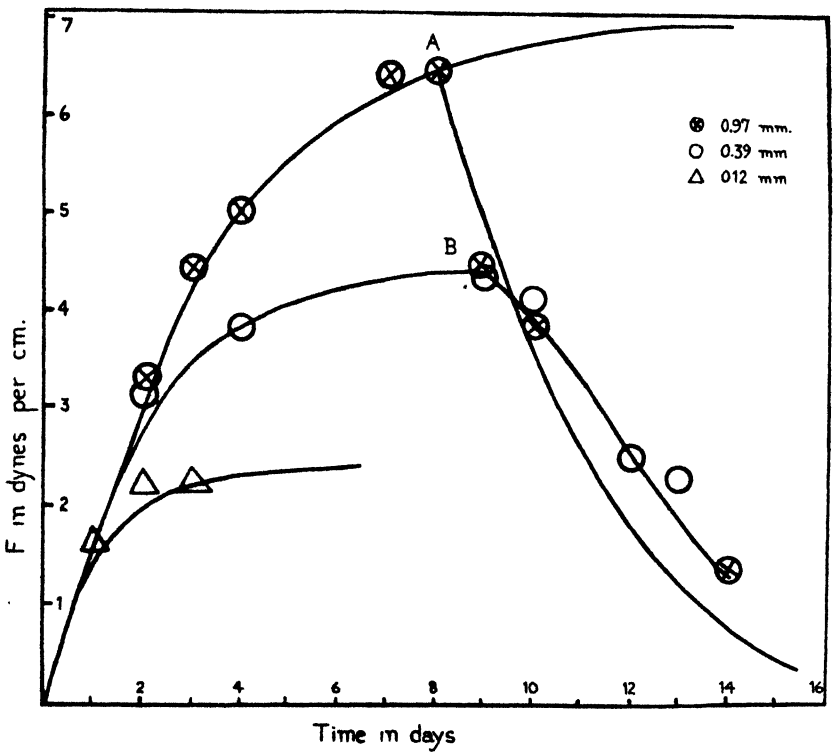

FIG. 4. THE SURFACE TENSION OF MERCURY IN HYDROGEN

The hydrogen was passed over the glowing platinum wire D, joined to steel electrodes E E′, the lower one of which hung in mercury; in this way no sag occurs when the wire is heated. On leaving D the gas passed over phosphorus pentoxide and then through a tube immersed in liquid air.

Hydrogen was admitted to the drop at various pressures and the surface tension was measured as before. Between each run the whole apparatus was thoroughly degassed (heated as before), a fresh mercury surface was prepared, and the constancy of the surface tension of the latter was checked. It was found that a very slow decrease in surface tension occurred, the

experiments lasting several days. At low pressures the final value of the surface tension decreased with increasing pressure, but as the pressure of hydrogen was increased the rate of decrease fell off, and from 8 to 100 mm. no change was observed (figure 4). A number of runs were made at these higher pressures, and no fall in surface tension occurred during a week's observation.

THE THEORY OF THE FALL OF SURFACE TENSION IN HYDROGEN

The simplest assumption is that the slow fall in surface tension is accompanied by a slow adsorption, i.e., that not all the hydrogen molecules which strike the surface are adsorbed. We may speak therefore of an activation necessary for adsorption. Various possibilities may then be considered: a molecule may require activation before it is adsorbed, necessary to mount the energy hump on the intermolecular energy distance diagram (2); since mobility is possible on the surface, molecules may become adsorbed by striking those already on the surface, so that adsorption would be possible on other than the free space of Langmuir's theory; similarly, collisions between molecules on the surface may cause desorption, which may also result from collisions between molecules in the bulk and surface phases, if the pressure is sufficient. The bulk material of the adsorbent is usually looked upon as a perfect energy reservoir, but an important factor will be the rate of interchange of energy between the molecules of adsorbent and the adsorbed molecules.

If we consider the most probable of these possibilities, we may suppose that a fraction θ of the surface is covered, and that there are n molecules per square centimeter when the gas pressure is p. The rate of adsorption in molecules per second is then

$$(1-\theta)p(2\pi mkT)^{-\frac{1}{2}}\alpha + \theta p(2\pi mkT)^{-\frac{1}{2}}\beta$$

where the first and second terms refer to the bare and covered surface, respectively, and where α and β are the fractions of the impinging molecules which are adsorbed. If the activation is thermal, α and β will be of the form $e^{\frac{-k_1}{T}}$, $e^{\frac{-k_2}{T}}$, where k_1 and k_2 are constants. Similarly the rate of desorption is $\gamma\theta$, where γ, for activated desorption, is of the form $Be^{\frac{-k_3}{T}}$, where B and k_3 are constants.

If A is the area occupied by a molecule for a condensed film, then $\theta = nA$, and

$$\frac{dn}{dt} = (1-nA)\alpha p(2\pi mkT)^{-\frac{1}{2}} + nA\beta p(2\pi mkT)^{-\frac{1}{2}} - \gamma nA$$

or

$$\frac{dn}{C-Dn} = dt$$

where

$$C = \alpha p(2\pi mkT)^{-\frac{1}{2}}$$

$$D = \alpha pA(2\pi mkT)^{-\frac{1}{2}} + \gamma A - p(2\pi mkT)^{-\frac{1}{2}}A\beta$$

Hence

$$n = \frac{C}{D}(1 - e^{-Dt})$$

since $n = 0$ when $t = 0$ 1

Let F be the lowering of the surface tension of the mercury. Then $F = \sigma_0 - \sigma$, i.e., F is the surface pressure of the hydrogen film (σ_0 and σ are the surface tensions of pure mercury and of mercury in the presence of hydrogen). We may suppose that the surface film of gas behaves as a two-dimensional gas, which, owing to the surface forces, is more imperfect than the bulk material. Thus we may write

$$F = nkT + \delta n^2 + \ldots \qquad 2$$

The first term in the expansion may be called the kinetic pressure, the second the cohesive pressure (actually a tension). For the analogous case of a three-dimensional gas we may write

$$p = \frac{kT}{V - b} - \frac{A}{V^2}$$

where V is the volume per molecule, and b and A are constants. Phillips (10) has shown that the last term retains the same form independently of the law of force assumed. Thus n in equation 2 will be the true surface concentration only when this is small; moreover δ will be negative, and this is the result obtained below. It is interesting to note that for most pure liquids σ is expressible in the form

$$-\sigma = nkT - \delta n^2$$

where n is of the right order (10^{15}), the decrease in surface tension as temperature is increased being due, on this view, to the increase in surface pressure and to a smaller extent to the change in cohesion.

On inserting the value of n found in equation 1 in equation 2 we obtain

$$F = \frac{C}{D}kT(1 - e^{-Dt}) + \delta\frac{C^2}{D^2}(1 - e^{-Dt})^2$$

The experimental results for low pressures can in fact be fitted to a curve of the type

$$F = H(1 - e^{-Dt}) + J(1 - e^{-Dt})^2$$

This gives

$$\frac{dF}{dt} = De^{-Dt}\left[H + 2J(1 - e^{-Dt})\right]$$

Hence $\frac{dF}{dt} = 0$ when $t = \infty$, F having then the value $H + J$, or when

$$e^{-Dt} = 1 + \frac{H}{2J}$$

When $H = -2J$ these two points coincide; in other cases there is a small hump in the curve, giving

$$F_{max} = -\frac{H^2}{4J}$$

Since this does not correspond to anything physical and is due to the omission of higher terms in the equation for F, a better fit can be obtained by making $H = -2J$; this limitation is supported by the fact that on solving the curves without it a rough fit is obtained, except for the region of the hump, giving values of $-H$ between 1.5 and 2. When $H = -2J$ a good fit is secured throughout.

Hence we shall take

$$\begin{aligned} F &= -2J(1 - e^{-Dt}) + J(1 - e^{-Dt})^2 \\ &= -J(1 - e^{-2Dt}). \end{aligned}$$

This is easily solved by taking two points at times t_1 and t_2, such that $t_2 = 2t_1$. Then if

$$e^{-2Dt_1} = x$$

$$F_1 = J(x - 1) \qquad F_2 = J(x^2 - 1)$$

or

$$x = \frac{F_2 - F_1}{F_1} \qquad J = \frac{F_1^2}{F_2 - 2F_1}$$

The smooth curves in figure 4 were obtained in this way. The values of J, D, and $n_\infty = -2J/kT$ are given in table 1. The trend of D is interesting; it shows that $\beta > \alpha$.

The free motion of hydrogen on mercury is very probable, especially in view of the other evidence which shows that adsorbed molecules have a lateral mobility (5, 15). Burdon states that "it is difficult to picture the mechanism by which anything much less than a contiguous layer of molecules could appreciably affect the surface tension." This, however, neglects the motion of the adsorbed molecules in the surface.

At a pressure of 6 mm. a curve was obtained below that at a pressure of 0.39 mm., and above 8 mm. no change in surface tension was observed. This unexpected result can perhaps be interpreted in terms of deactivation by collision, and bears an apparent analogy to explosion limits. It would seem that no hypothesis other than some type of activation can account for the slow fall of surface tension in hydrogen. For even if slow solution occurred, and the surface film were rapidly established, there would be no reason why the composition of the surface should not remain the same, and presumably the surface tension would be constant. There is the possibility that a film is held by weak adsorption, and that this then forms a stronger union with the mercury, when equations similar to the above would be obtained, the weakly adsorbed film replacing the bulk gas as a reservoir of molecules. Mercury and hydrogen combine only when the molecules are excited, but when once formed the molecule HgH is fairly

TABLE 1

p	J	D	$n \times 10^{-14}$
mm			
0 97	−6 94	0 1623	3.56
0 39	−4 41	0 2458	2 26
0 12	−2 39	0 4380	1.23

stable, with an energy of dissociation of 8500 calories per gram-molecule (9). It is possible that the activation is due to external radiation.

A study was also made of desorption from the surface. According to the above, if adsorption is stopped at the point t_1,

$$F_{t_1} = -2J(1 - e^{-Dt_1}) + J(1 - e^{-Dt_1})^2$$

$$= n_{t_1}kT + \delta n_{t_1}^2$$

If now t is measured from this point as a new zero,

$$\frac{dn}{dt} = -Gn$$

where $G = \gamma A$. Hence

$$n = n_0 e^{-Gt}$$

where n_0 is the value of n at the point $t = 0$, the point at which desorption began. As before, equation 2 gives

$$F = n_0 kTe^{-Gt} + \delta n_0^2 e^{-2Gt}$$

Since n_0 for the desorption is the same as n_{t_1} for the adsorption curve, the equation for desorption will therefore be

$$F = H'e^{-Gt} + J'e^{-2Gt}$$

where

$$H' = -2J(1 - e^{-Dt_1})$$

and

$$J' = J(1 - e^{-Dt_1})^2$$

it is asymptotic to the axis of time.

The desorption curve contains therefore only one unknown constant, G, as the others can be calculated from the adsorption curve. G is easily found by taking one point on the desorption curve at t_2, and solving for

$$e^{-Gt_2} = x$$

as the admissible root of the equation

$$F_{t_2} = H'x + J'x^2$$

TABLE 2

p	H'	J'	G
mm.			
0.97	10 09	3 67	0 4311
0.39	8.82	4.41	0.3575

In this way the curves for 0.97 and 0.39 mm. were obtained, desorption starting at the points A and B, when the apparatus was pumped down to a hard vacuum, and it is noteworthy that in these curves H' and J' were calculated from the curves for adsorption. Moreover it will be seen from table 2 that the G's are nearly the same, as they should be, and that they are greater than the corresponding D's, as they should be if $\beta > \alpha$.

THE EFFECT OF ILLUMINATION

Mercury vapor excited by light of wave length 2536 A.U. can dissociate hydrogen to atoms by a mechanism which is probably represented by

$$Hg' + H_2 \rightarrow HgH' + H$$

the dashes indicating excited molecules. The HgH′ reverts to the normal state with the emission of a band spectrum, and may then dissociate. A tube was fitted on the apparatus at right angles to the mercury surface and

the end was blown out very thin. This thin spherical end was surrounded by a tube which could be evacuated, and to the end of this tube was waxed a quartz plate. By adjusting the pressure on the outside of the thin end, collapse was avoided. Light was shone on to the mercury surface from a Pyrex mercury vapor lamp with a thin window (13). The lamp was cooled by a strong air blast, as the cold mercury vapor absorbs only the center of the line, and the waxed quartz plate was also cooled. No immediate effect was observed, but the rate of decay after illumination was greater than normally; thus with a pressure of 1 mm. the surface tension fell 7 dynes in three days instead of 4.5 dynes, after 10 minutes illumination; after an hour's illumination it fell 7 dynes in one day. It seems probable that this effect is due to HgH molecules which have reverted to the normal state. These would be easily adsorbed as one end would be "soluble" in mercury.

SUMMARY

The surface tension of mercury was determined by measurements on a flat drop, using a method of defining the top surface of the drop which was free from error. The mean value of 500.3 dynes per centimeter at 16.5°C. was obtained. The fall of the surface tension in hydrogen at pressures from 0 to 100 mm. was studied and interpreted theoretically. The surface was illuminated with light from a mercury vapor lamp. No immediate effect was noticed, but the surface tension fell more rapidly than normally.

My thanks are due to Professor Whytlaw Gray, F.R.S., for encouragement and to Imperial Chemical Industries Ltd. for a grant which defrayed part of the cost of the apparatus.

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COMMUNICATION TO THE EDITOR

EFFECT OF SULFATED FATTY ALCOHOLS IN THE COLORIMETRIC DETERMINATION OF pH

In This Journal (J. Phys. Chem. **37**, 1001 (1933)) Neville and Jeanson state that they used standard indicators to determine colorimetrically the pH of solutions containing Gardinol CA. Since no mention is made of the errors which may be encountered in utilizing this method, it appears advisable to point out certain limitations which exist.

We have examined the effect of Gardinol CA (sodium salt of sulfated technical oleyl alcohol), and Gardinol WA (sodium salt of sulfated technical lauryl alcohol), on a number of common indicators in buffered solutions and have found that the fat alcohol sulfates exert a specific effect on most indicators, which is frequently a source of appreciable error. Our method was as follows: 5 cc. of the buffer solution, prepared by the specifications of Clark and Lubs (W. M. Clark: The Determination of Hydrogen Ions, pp. 192–202. Williams & Wilkins Co., Baltimore (1928)), was diluted with 5 cc. of water and 0.5 cc. of the indicator solution (La Motte) and the pH observed in the La Motte comparator. For comparison, 5 cc. of the buffer solution was diluted with 5 cc. of a fat alcohol sulfate solution and 0.5 cc. of the indicator and the apparent pH determined as above. Measurements were made at three or more values in the range covered by each indicator.

The observed errors in all of the determinations made in the presence of fat alcohol sulfates were on the acid side of the values obtained for the corresponding buffer solutions free of the fat alcohol sulfates. The comparisons show that in 0.5 per cent sodium lauryl sulfate solutions the error in the observed pH value, using cresol red (acid), methyl red, bromthymol blue, and thymol blue, is greater than 1.0; using meta cresol purple, bromcresol green, and bromcresol purple, is greater than 0.5; using La Motte yellow, and chlorphenol red, is greater than 0.2; using cresol red (alkaline), is less than 0.2; and using phenol red and La Motte purple, is negligible. At a 5.0 per cent concentration of this fatty alcohol sulfate, all of the indicators are in error. With 0.5 per cent sodium oleyl sulfate solutions, the error in the observed pH value, using bromthymol blue, is greater than 1.0; using cresol red, methyl red, and thymol blue, is greater than 0.5; using meta cresol purple, bromcresol green, bromcresol purple, and chlorphenol red, is greater than 0.2; using phenol red and cresol red, is less than 0.2; and using La Motte yellow and La Motte purple, is negligible. Electro-

metric measurements have shown that no change in pH occurs when a fatty alcohol sulfate solution is added to a buffer solution in the manner used in obtaining these results. The technical sodium lauryl sulfate used in these experiments was of 75 per cent and the technical sodium oleyl sulfate was of 50 per cent strength. Both products were slightly alkaline to phenol red, but the amount of alkali present was negligible when compared with the concentration of the buffers.

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NEW BOOKS

Les fondements de la théorie de la relativité générale. Théorie unitaire de la gravitation et de l'electricité. Sur la structure cosmologique de l'espace. By A. EINSTEIN. Translated from the German by Maurice Solovine. 111 pp. Paris: Hermann et Cie, 1933. Price: 35 francs.

The first two sections of this small volume dealing with general relativity and with the unitary theory of electricity and gravitation are translations of two papers published, the first one in 1916, the second one in 1931. As far as these two articles are concerned, the present volume will be of use mainly to those who prefer French to German or to whom this translation is more easily accessible than the original publications.

The third section on the cosmological structure of space is translated from a manuscript prepared in September, 1932. Einstein concludes that in a dynamic theory of the universe, the existence of an average density of matter different from zero must not be related theoretically to a curvature of space but to a spatial expansion. In the light of our present knowledge, there is no sure indication of spatial curvature, positive or negative.

F. H. MACDOUGALL.

Die physikalische Chemie der Kesselstein Bildung und ihrer Verhütung. Second revised and enlarged edition. By R. STUMPER. 74 pp.; 18 illustrations. Stuttgart: Ferdinand Enke, 1933. Price: paper, 5.30 R.M.; as part of collection, 4.80 R.M.

It is only three years since the first edition of this pamphlet appeared, which is an indication of how well it has been received. In it the author has collected the most plausible theories of boiler scale formation and methods of combatting it. It is a clear exposition of the physico-chemical equilibria of scale formation, the formation of solid and crystalline phases in supersaturated solutions, and an explanation of the effect of evaporation and colloids on scale formation. This edition discusses silicate scales, the solubility of scale constituents at operating boiler temperatures and pressures, and the dynamics of carbonate scale formation.

Old and new methods of scale prevention by shifting of chemical equilibria, by means of colloids, mechanically, and electrically are critically considered.

Throughout this pamphlet are given excellent tables of data, graphs, illustrations, some calculations, and many literature references. The subject matter is very well treated from the theoretical standpoint. Practical calculations and applications would make the pamphlet more useful to the practicing engineer.

CHARLES A. MANN.

The Conductivity of Solutions. Second edition. By CECIL W. DAVIES. viii + 281 pp.; 32 figs. New York: John Wiley and Sons, Inc., 1933. Price: $4.00.

This book may be recommended as an interesting, easily readable, but hardly adequate presentation of modern theories of the electrical conductance of solutions. The standpoint of the author seems to be that chemists need not understand the equations of Debye or of Onsager but should only be concerned with their success in

predicting experimental results. In harmony with this is the fact that the author evidently does not require his readers to possess mathematical knowledge beyond algebra and analytic geometry. In spite of the importance of the subject in connection with the measurement of conductivity, the book does not contain anything approaching an adequate treatment of inductance, capacity, and polarization effects.

Nevertheless there is much in this text book that deserves high praise and that can be read with profit by both beginners and advanced students. We refer to the many applications of Onsager's equation, the discussion of the solvent correction, the evaluation of the equivalent conductance at zero concentration and finally the use of conductance methods in solving analytical problems in pure and technical chemical research.

F. H. MacDougall.

Bearing Metals and Bearings. American Chemical Society Monograph Series, No. 53. By W. M. Corse. 6 x 9 in.; 383 pp. New York: The Chemical Catalog Company, Inc., 1930. Price: cloth, $7.00.

The author has surveyed the literature on bearing metals and bearings and has collected into one volume bibliographic references to the widely scattered publications in different languages and in many journals, the more important articles being abstracted. Part I (25 pages) presents a brief but interesting history of the development of bearing metals and bearings. This part serves to acquaint those not familiar with this field of work with some of the important subjects.

Part II (106 pages) contains more than a thousand bibliographic references to articles on bearing metals, sliding-contact bearings, friction, and lubrication. The metals included are the white metals, the bronzes, and the graphite bearing metals. The bibliographic references are arranged under appropriate main and subheadings and cover the literature through 1928.

Part III (108 pages) contains two hundred thirty-four abstracts of selected papers. These abstracts were specially prepared and give quite completely the important information in the original articles. Part IV contains sixteen tables showing the properties of bearing metals.

This volume is a valuable contribution to workers and students in this field. In looking up the published information on this whole field or on any special phase of it, much time can be saved by making use of the material which Corse has collected and put into convenient and usable form. The author index contains about seven hundred names, and the subject index provides an easy means of finding the information on some two hundred subjects.

Oscar E. Harder.

Grundlagen der Photochemie. By K. F. Bonhoeffer and P. Harteck. 295 pages; 73 figures; 30 tables. Dresden and Leipzig: Theodore Steinkopff, 1933. Price: bound, 25 R.M.; unbound, 24 R.M.

In the three or four decades during which the study of chemical kinetics has been intensively pursued, it has become increasingly evident that there is no golden road to knowledge along which progress takes an easy course. This is equally or more true of photochemical kinetics. The technique is difficult; the theory, involving several domains of physics and chemistry, is complicated and incomplete. The Einstein law of photochemical equivalence and its experimental verification marked a milestone of substantial achievement; the application of the principles of modern spectroscopy to photochemical phenomena ushers in the newest phases of photochemistry.

It is these principles and their detailed application to various photochemical

reactions that are admirably introduced and treated in the present work. Experimental procedure is wholly omitted nor is any attempt made to give a complete citation of all photochemical reactions that have been investigated, though the most important ones, naturally, are discussed in applying theoretical considerations to them.

The first chapter contains a list of gaseous and liquid reactions of which the quantum yields have been determined both in direct and in sensitized photochemical reactions. The second chapter, entitled "The Photochemical Primary Process," is introduced by a splendidly condensed general treatment of atomic and molecular light absorption, continuous and discrete spectra, dissociation and predissociation, followed by the application of these principles to many photochemically important substances for which tables of absorption spectra and diagrams of energy levels are given. The third chapter deals with the photochemical secondary or thermal reactions that follow the primary act. The final chapter treats rather fully the complete kinetics of about a dozen of the most fully investigated photochemical reactions.

After examining this excellent treatment of photochemistry from the modern standpoint, one cannot fail to be impressed by the fact that in spite of its greater experimental difficulties photochemistry has not only repaid thermal kinetics for all that was borrowed, but has enriched it with a knowledge of atomic chemistry that will enable both to advance with enhanced certainty and rapidity, arduous though the way may be.

S. C. LIND.

Liquid Crystals and Anisotropic Melts. A General Discussion held by the Faraday Society. 25 x 16 cm.; iv + 204 pp. London: Gurney and Jackson, 1933. Price: 12/6d.

The present volume, reprinted from the *Transactions of the Faraday Society*, contains twenty-four papers and a general discussion. Two papers, that on the connection between the x-ray patterns of gases and true liquids, and the contribution of Bernal and Fowler on water, are particularly interesting. Water is, we presume, nearly as good a liquid as ever was, and our feeling is that the subject matter of the volume should have been extended to include the most interesting question of structure in so-called isotropic liquids. The book would then have possessed a uniformity which its contents at present belie.

There is no question about the value of the book as a whole. The subject has previously received attention from Continental scientists alone, as reference to a recent volume of the *Zeitschrift für Kristallographie* shows. The names of Vorländer, Kast, Ornstein, Rinne, Zocher, and Ostwald are sufficient guarantee to the authoritative nature of the volume under review. In addition there are the English contributors, Bernal, W. H. Bragg, Crowfoot, Fowler, Malkin, and Lawrence.

Ornstein and Zocher discuss rival theories of liquid crystals; Rinne emphasizes their biological importance. Lawrence makes a valuable contribution to the study of the lyotropic mesomorphs. Until these discussions, little or no study of the true crystalline phases of liquid–crystal forming substances had been made. Bernal and Crowfoot have performed a valuable service in remedying this state of affairs. It is only by comparison of the densities in the solid and liquid phases that one may obtain clues as to the modifications of grouping which take place on melting. If the arrangements in the true solid are unknown, speculations about arrangements in true liquids or the mesophases of liquid crystals become mere guess work.

The work of Bernal and Fowler is of far-reaching importance. Lack of space prevents anything like an adequate summary of their paper; briefly, however, their

achievements are these. The accepted crystalline structure of ice has been modified. The unit cell is very much bigger than that found by Barnes and the structure is molecular: four molecules are arranged in rough tetrahedral fashion round a central fifth. This arrangement and various developments of it in space, is, in conjunction with Prins's theory, the basis of their explanation of the x-ray diffraction patterns of water and their variation with temperature. Water changes from something roughly ice-like at low temperatures to a quartz-like structure at ordinary temperatures. Further heating tends to produce close packing.

The whole volume is of great value to those interested in structural physics and chemistry, particularly from the point of view of the transition from solid to liquid. Need the binding of the *Discussions* be quite so flimsy?

J. T. RANDALL.

I. THE ADSORPTION OF ALKALI HYDROXIDES BY SILICA GEL IN THE PRESENCE OF AMMONIA AND AMMONIUM SALTS[1]

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In a preliminary communication (4) various factors affecting the adsorption of cations from ammoniacal solution by silica gel have been mentioned. It has been pointed out that equilibrium may not be reached even after a long time of shaking, and that during the experiment the external and internal surface of the gel may change, owing to the dissolving effect of the alkali. Since the alkali hydroxides form soluble silicates, it might be expected that with these bases adsorption equilibrium is attained more quickly than in cases where the cations form slightly soluble silicates. In this paper the adsorption of sodium and potassium hydroxides, also in the presence of ammonia and ammonium salts, and of ammonia by silica gel is described.

SILICA GEL USED

The same gel was used as in the previous work (4). It was purchased from the Silica Gel Corporation and had originally been prepared by a modification of McGavack and Patrick's method (5). It was purified in this laboratory with nitric acid and finally by electrodialysis as described before (4). After drying at 350°C. it contained 3 per cent of water. In agreement with results of Bartell and Almy (1) it was found that on heating the gel to 900°C. its activity decreased considerably (40 to 50 per cent). In addition, its speed of solution in alkaline liquids had decreased markedly. In agreement with van Bemmelen's work (7) no indication was obtained that adsorbed water is chemically bound, but rather that it covers the surface of capillary walls as a result of capillary action and then fills the capillaries themselves. Figure 1 gives the results of experiments in which the gel was kept at various water vapor tensions for different times. The typical S shaped curves are found only at or close to equilibrium conditions; with

[1] From a thesis submitted by Vernon A. Stenger to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1933.

[2] J. T. Baker Fellow in Analytical Chemistry, 1932–1933.

insufficient time of standing the curves representing the amount of water adsorbed at various vapor tensions have a different shape. The ordinate in figure 1 indicates the number of moles of water adsorbed per mole of silica gel; the abscissa gives the relative vapor tension.

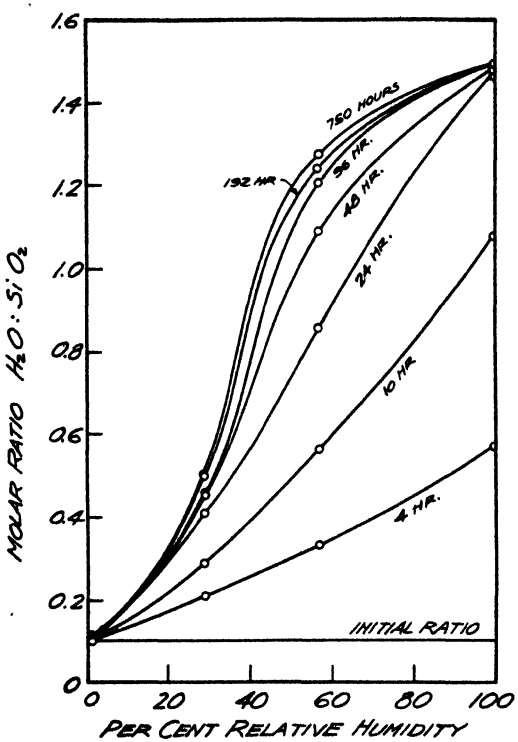

FIG. 1. ADSORPTION OF WATER

PROCEDURE AND ANALYSIS

The experiments were carried out as described before (4), the samples being shaken at room temperature (around 25°C.) on an eccentric rotary shaker revolving at 160 R.P.M.

The amount adsorbed was determined by analysis of the supernatant liquid or by extraction of the quickly washed gel with a known volume of standard acid; usually both procedures were followed. The total amount of base adsorbed was found by standard volumetric procedures, whereas ammonia in the presence of other bases was determined by oxidation with a new stable standard reagent, calcium hypochlorite. The details of this method will be described elsewhere.

Former workers who have studied the adsorption of bases by silica gel have not considered the amount of adsorbent going into solution during

the experiments. In all our work the amount dissolved has been determined by transferring the sample of gel, after extraction with acid and rinsing, to a porcelain crucible and igniting for 1½ hours at 900°C. The water content of the original sample was determined in a similar way.

EXPERIMENTAL

In order to get comparable results the same speed of shaking, the same size of the gel, and the same temperature should be maintained during the work. The speed of adsorption and of solution appeared to increase with increasing speed of shaking and decreasing size of the particles of the gel. The adsorption of ammonia and the solubility in dilute ammonia solutions were determined at 5°, 25°, and 45°C., respectively. The adsorption of the base decreases, but the speed of solution increases much more markedly with increasing temperature.

Adsorption of sodium hydroxide and potassium hydroxide

Some results on the relation between the time of shaking and the amount of base adsorbed and amount of gel gone into solution are given in table 1. The number of milliequivalents of base adsorbed per 1 g. of original gel have been corrected for the amount of gel dissolved during the experiment.

With the 0.0057 *N* sodium hydroxide solution, adsorption equilibrium seems to be reached after one hour of shaking, although more gel is going into solution on prolonged time of contact. With the stronger solution equilibrium has not been attained even after four hours of shaking, whereas more than 50 per cent of the gel had gone into solution after that time. With potassium hydroxide similar results were obtained.

In the final experiments the adsorption isotherm was determined after four hours of shaking. The results plotted in figure 2 show the abnormal shape of the curve, if the data are not corrected for the amount of gel dissolved. In figure 3 the amounts of sodium and potassium hydroxides, ammonia, and calcium hydroxide adsorbed after four hours of shaking and corrected for the dissolved gel are plotted.

Adsorption of ammonium hydroxide

The adsorption of ammonium hydroxide was studied in considerable detail, since in later experiments the adsorption of cations from ammoniacal solution was investigated. Preliminary experiments showed that adsorption equilibrium is virtually established within two hours, although on longer shaking more gel is going into solution.

Table 2 gives the percentage of gel going into solution and the amount of ammonia adsorbed after two hours of shaking. The reported adsorption data have been corrected for the dissolved amount of gel.

The desorption of the ammonia was studied by washing the gels continuously with water for various periods of time. Even after sixty days all the gels contained some ammonia, but only of the order of 3 to 4 per

TABLE 1

Adsorption of sodium hydroxide and solubility of gel in the alkaline solution

0.5 g. of gel; 100 cc. of solution

TIME SHAKEN	FINAL CONCENTRATION OF NaOH	GEL DISSOLVED	NaOH ADSORBED (NOT CORRECTED FOR SOLUBILITY OF GEL) MILLIEQUIVALENTS PER GRAM OF GEL		NaOH ADSORBED (CORRECTED FOR SOLUBILITY) MILLIEQUIVALENTS PER GRAM OF GEL	
			From analysis of solution	From extraction of gel	From analysis of solution	From extraction of gel
Original concentration of NaOH = 0.00566 *N*						
hours	*N*	*per cent*				
0.5	0.0033	1.8	0.48	0.47	0 49	0.48
1	0.0030	2.85	0 54	0.54	0.55	0.56
2	0.0030	4 8	0.54	0.54	0.57	0 56
4	0.0032	6 5	0.50	0.50	0.53	0 53
6	0.0031	6.75	0.51	0.50	0 55	0 54
12	0.0031	7.3	0.51	0.51	0 55	0.55
Original concentration of NaOH = 0.0566 *N*						
0.5	0.0513	7 0	1.07	1 00	1 15	1 08
1	0 0509	18 9	1.14	1 09	1 41	1 34
2	0.0511	32.7	1.10	1 04	1 64	1 55
4	0 0525	56.4	0 82	0 77	1 89	1.77

TABLE 2

Adsorption of ammonia

0.5 g. of gel per 100 cc. of solution; 2 hours of shaking

FINAL CONCENTRATION OF NH_3	GEL DISSOLVED	NH_3 ADSORBED IN MILLIEQUIVALENTS PER GRAM (CORRECTED FOR SOLUBILITY)	
		From analysis of solution	From extraction of gel
N	*per cent*		
0.00680	4.1	0 52	0.51
0.0119	5.0	0 68	0.67
0.0207	4.4	0.85	—
0.0443	5.7	1 12	—
0 0696	7.2	1 29	1.28
0 0923	7 4	1 56	1.48
0.1625	9 2	1.74	1.74
0.24	10.0	2 05	1.96
0.49	12 3	2.14	2.31
0.99	14.4	—	2.80
1.98	17.9	—	3.48

cent of the original amount adsorbed. It is interesting that especially in the first periods of the desorption the gels lost fairly much in weight, thus showing that the adsorbed ammonia is given off in the form of ammonium silicate.

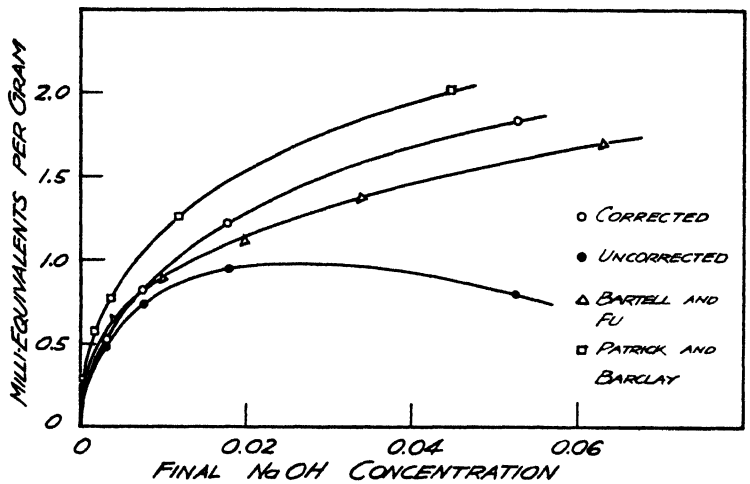

FIG. 2. ADSORPTION OF SODIUM HYDROXIDE

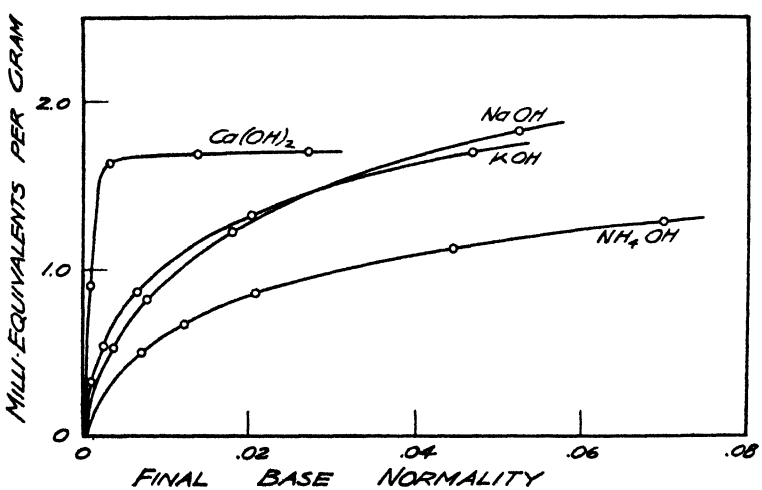

FIG. 3. ADSORPTION OF VARIOUS BASES

Experiments have been made in which the adsorption of ammonia at various concentrations was determined in the presence of varying amounts of ammonium chloride. The adsorption of ammonia (no chloride is removed from the solution) appeared to be entirely independent of the am-

monium salt concentration in the solution, although, as might be expected, the solubility of the gel is markedly decreased in the presence of an excess of ammonium ions.

The adsorption of potassium hydroxide in the presence of potassium and ammonium salts

Potassium salts favor the adsorption of potassium hydroxide, as is shown by some figures given in table 3.

Ammonia and potassium chloride. On shaking an aqueous solution of potassium chloride with silica gel a slight hydrolytic adsorption of the base takes place, no chloride being removed from the solution. This result is in agreement with the findings of Bartell and Fu (2). In the presence of ammonium hydroxide a strong adsorption of potassium hydroxide is found, whereas the ammonia adsorption decreases markedly. Experiments have

TABLE 3

Adsorption of potassium hydroxide in the presence of potassium chloride

(4 hours)

CONCENTRATION OF KOH		CONCENTRATION OF KCl	GEL DISSOLVED	KOH ADSORBED IN MILLIEQUIVALENTS PER GRAM (CORRECTED FOR SOLUBILITY)	
Original	Final			From analysis of solution	From extraction of gel
N	*N*	*N*	*per cent*		
0 005	0 0025	0	5 8	0 55	0 55
0 005	0 0010	0 1	4 4	0 85	0 85
0.005	0.00067	0 5	3 6	0.91	0 94
0 05	0 0466	0	55 7	1.78	1.65
0 05	0.0468	0.1	58 4	1.76	1 69
0.05	0 0464	0.5	61 8	2.12	2 03

been carried out in various mixtures of ammonia and potassium chloride over periods of time up to twelve hours. Adsorption equilibrium was attained after four hours of shaking. The results of 4-hour experiments are given in table 4 and plotted in figure 4.

It is evident that the potassium and ammonium ions compete for positions at the surface of the gel. If the concentration of the ammonium ions is increased, the adsorption of potassium hydroxide is strongly reduced. Comparison of the results given in tables 4 and 5 brings this fact out very clearly.

If, on the other hand, the concentration of the ammonium ions is strongly decreased by working with mixtures of potassium hydroxide and ammonia, the adsorption of the latter is reduced markedly. The adsorption of ammonia from a 0.05 *N* solution, for example, was 1.12 milliequivalents per gram; in the presence of 0.025 *N* potassium hydroxide it amounted to 0.35.

The adsorption of the potassium hydroxide increased from 1.32 milliequivalents in the absence of ammonia to 1.43 milliequivalents in the presence of 0.05 N ammonia.

DISCUSSION OF THE RESULTS

It is evident that in the adsorption of potassium and sodium hydroxides a primary adsorption of hydroxyl ions takes place, the latter ionize the surface of the gel, and a secondary adsorption of the alkali ions takes place. If the concentration of the alkali ions is increased by adding them in the form of a neutral salt to the alkaline solution, an increased adsorption of the base is noticed (see table 3), since less energy is required to withdraw the alkali ions from the solution. The adsorption curves as determined by Patrick and Barclay (6) and by Bartell and Fu (2) have no exact signifi-

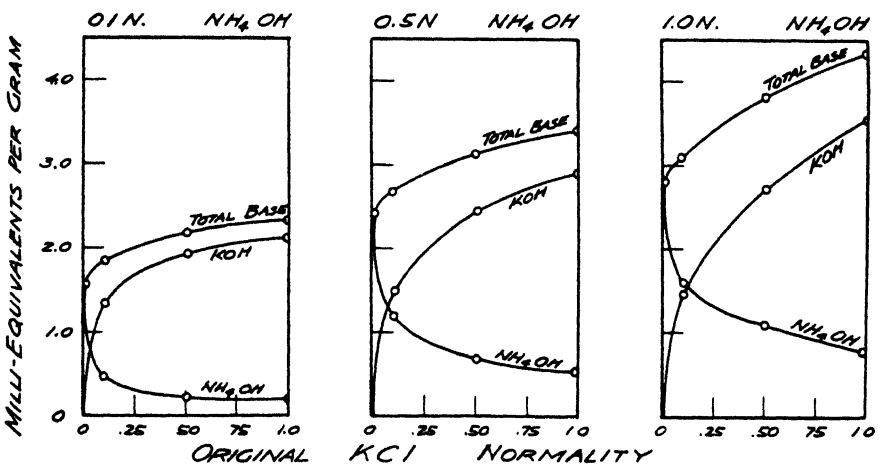

FIG. 4. ADSORPTION FROM AMMONIUM HYDROXIDE–POTASSIUM CHLORIDE MIXTURES

cance, since their data have not been corrected for the loss in solubility of the gel. It should be mentioned that this correction is smaller under their experimental conditions than in our work, however. In solutions of the bases more concentrated than about 0.03 N, the solubility is so pronounced that no adsorption equilibrium can be attained. The surface of the gel is changing constantly and new layers of the gel are exposed continuously to the solution. In addition, it should be realized that the dissolved silicate is hydrolyzed, resulting in a decrease of the hydroxyl ion concentration of the alkali hydroxide in the solution. From our results one may infer that the adsorptions of sodium and potassium hydroxides by silica gel are of the same order, but no more exact conclusions can be drawn.

The speed of adsorption of ammonia is greater than that of the strong alkali hydroxides. This might be caused by a more rapid diffusion of the

TABLE 4

Adsorption from ammonia–potassium chloride mixtures

0.5 g. of gel; 100 cc. of solution; 4 hours of shaking

ORIGINAL CONCENTRATION OF NH_3	KCl CONCENTRATION	FINAL CONCENTRATION OF BASE	GEL DISSOLVED	BASE ADSORBED IN MILLIEQUIVALENTS PER GRAM (CORRECTED)				MOLAR RATIO NH_3:KOH ADSORBED
				Total base		NH_3	KOH	
				From solution	From extraction			
N	*N*	*N*	*per cent*					
0.099	0	0 0914	9 5	1.66	1.56	1.56	0	
0.099	0.1	0.0904	9.8	1.88	1 84	0.49	1.35	0.36
0.099	0.5	0.0893	11.2	2 16	2.18	0.24	1.94	0.12
0.099	1.0	0.0886	11.4	2 33	2.32	0 20	2 12	0.09
0.50	0		17.5		2 42	2.42		
0.50	0.1		21 3		2 67	1.19	1.48	0.80
0.50	0.5		26 3		3 12	0.67	2.45	0.27
0.50	1.0		27.9		3 42	0.51	2.91	0.17
1.0	0		23 2		2 80	2 80		
1 0	0.1		30 0		3 08	1.61	1.47	1.1
1 0	0.5		37.7		3 80	1.09	2 71	0 40
1.0	1.0		41.9		4.35	0.79	3.56	0.22

TABLE 5

Adsorption from ammonia–ammonium chloride–potassium chloride mixtures

0.5 g. of gel; 100 cc. of solution, 4 hours of shaking

ORIGINAL CONCENTRATION OF NH_3	CONCENTRATION OF NH_4Cl	CONCENTRATION OF KCl	GEL DISSOLVED	BASE ADSORBED IN MILLIEQUIVALENTS PER GRAM (CORRECTED FOR SOLUBILITY)			MOLAR RATIO NH_3:KOH ADSORBED
				Total base	NH_3	KOH	
N	*N*	*N*	*per cent*				
0.099	0.1	0	3.4	1 48	1.48		
0.099	0.1	0 1	4.0	1.61	1.10	0.51	2.15
0.099	0.1	0.5	4 4	1.77	0.64	1.13	0.57
0.099	0.5	0	2.3	1.48	1.48		
0 099	0.5	0.1	3 1	1.59	1 49	0.10	14.9
0 099	0.5	0.5	3.3	1.65	1 18	0.47	2.5
0 5	0.1	0	3 5	2.31	2 31		
0 5	0.1	0.1	7.9	2.42	1 88	0.54	3.5
0 5	0.5	0	2.9	2 35	2.35		
0 5	0.5	0.1	4.8	2.41	2.29	0.12	19.1
0.5	0.5	0.5	5.0	2.52	1.97	0.55	3.6
0.5	1.0	0	3.5	2.32	2.32		
0.5	1.0	0.5	3.9	2.50	2.28	0.22	10.4
1.0	0.5	0	4.7	2.80	2.80		
1.0	0.5	0.1	6.0	3.03	2.90	0.13	22.3
1.0	0 5	0.5	6.4	3.04	2.49	0.55	4.5
1.0	1.0	0	4.1	2.80	2.80		
1.0	1.0	0.5	4.9	2.98	2 74	0.24	11.4

ammonia into the interior of the gel. Some experiments were made in which the dried gels (containing 3 per cent of water) and those previously saturated with water vapor (containing 42 per cent of water) were used. After short periods of shaking, more ammonia was adsorbed by the dry gels, indicating that the ammonia diffuses more rapidly into the gel than water does. After two hours of shaking the same amounts of ammonia were adsorbed by both kinds of gel. Whereas addition of potassium chloride increases the adsorption of potassium hydroxide very markedly, no such effect was noticed upon adding an ammonium salt to the ammonia solution. The adsorption of the ammonia was found to be independent of the concentration of the ammonium salt. The adsorption is primarily a function of the hydroxyl ion concentration; by addition of an ammonium salt to the ammonia solution this concentration is strongly reduced. However, the product of $(OH^-)(NH_4^+)$ remains practically constant. From the fact that the ammonia adsorption is not affected by the concentration of ammonium salt in the solution, one might infer that the adsorption of the base is primarily a molecular and not an ionic one. However, the results of various experiments point in the direction that the ammonia is held in the ionized state. In the desorption experiments, for example, the ammonia was washed out in the form of ammonium silicate. The data presented in tables 4 and 5 show a primary adsorption of hydroxyl ions to take place, whereas the ammonium and potassium ions compete in the secondary adsorption. After this work had been concluded M. Berthon (3) published a note in which he mentioned that sodium hydroxide was adsorbed by silica gel from a mixture containing ammonia and sodium chloride. However, he did not consider the effect of the salt upon the adsorption of ammonia. It is seen from the figures in table 4 that the adsorption of the weak base is strongly reduced in the presence of potassium chloride. This does not necessarily mean that the potassium ions are more strongly adsorbed than the ammonium ions, because the latter are greatly outnumbered by the former. For example, in the experiment with 0.1 N ammonia and 0.1 N potassium chloride the ratio of NH_4^+ to K^+ is approximately 1:75. If the ammonium ion concentration is increased by addition of ammonium chloride (see table 5), about two to three times more ammonium than potassium hydroxide is adsorbed at the same ammonium and potassium ion concentration in the solution. This indicates that ammonium ions actually are more strongly held by the ionized silica surface than potassium ions.

It is interesting to notice that at a given ammonia concentration the ratio of ammonia to potassium hydroxide adsorbed is nearly a linear function of the ratio of ammonium to potassium ions in the solution (table 5), hence the total effect is mainly determined by the competition between the ammonium and potassium ions. However, table 5 also furnishes some evi-

dence that part of the ammonia is adsorbed in the molecular form. The molar ratio of ammonia to potassium hydroxide adsorbed with the same ratio of ammonia to potassium ions in the solution increases slightly but regularly with increasing ammonia concentration in the solution. The changes, however, are small, indicating that the ratio in which the two bases are adsorbed at the same hydroxyl ion concentration is mainly determined by the ratio of the concentration of the ammonium and potassium ions in the solution. It is easily understood then that in mixtures of potassium and ammonium hydroxides the adsorption of the latter is so strongly reduced.

SUMMARY

1. It is impossible to determine the adsorption of strong alkali hydroxides by silica gel with any degree of exactness, owing to their dissolving effect upon the gel. Our results indicate that the adsorption of potassium hydroxide is of the same order as that of sodium hydroxide.

2. The adsorption of ammonia is primarily ionic. Owing to the fact that it is a weak base, its adsorbability is found to be less than that of sodium or potassium hydroxide at the same analytical concentration in the solution.

3. Potassium salts increase the adsorption of potassium hydroxide, whereas ammonium salts do not affect the adsorption of ammonia.

4. The amount of total base adsorbed from a mixture containing ammonium and potassium ions is primarily a function of the hydroxyl ion concentration of the solution. The ratio in which ammonium and potassium hydroxides are adsorbed is mainly determined by the ratio of ammonium to potassium ions in the solution.

5. The secondary adsorption of ammonium ions is stronger than that of potassium ions.

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THE SOLUBILITY OF PHENOLS IN PROTEINS

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The investigations so far carried out on this subject (1) have shown that the germicidal power of a disinfectant is not determined by the magnitude of the partition coefficient, which measures the ratio of its solubilities in a *protein sol* and water. Thus, *p*-chlorophenol is five times as efficacious in disinfecting power as phenol, and yet the partition coefficients

$$\frac{\text{solubility in protein sols}}{\text{solubility in water}}$$

are of much the same order of magnitude, e.g., 4 and 3, respectively.

In the case of proteins in the precipitated or coagulated state, however, it has been found that there is a general parallelism between the germicidal powers of the phenols and their partition coefficients between proteins and water. This result was unexpected, as the normal physiological state of proteins in the cell is not a coagulum, but a *sol* or *gel*. Furthermore, the partition coefficients are much higher with protein coagulae than with colloidal solutions, such as egg albumin sols, or gels, e.g., ordinary gelatin; in the case of phenol the partition coefficient is 3 with sols and gels, and 12 with albumin coagulated by heat or by phenol itself. Similar results were obtained with cresol and chlorophenols.

The experimental work described in the present paper has been carried out with the object of discovering an explanation of these unexpected physico-chemical observations.

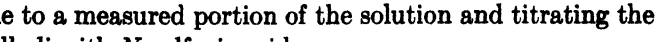
I. DISTRIBUTION OF CHLORAL HYDRATE AND PICRIC ACID BETWEEN PROTEINS AND WATER

In the first place, we have endeavored to ascertain whether such abnormalities apply to disinfectants and physiologically active substances other than phenols and cresols, and their halogen derivatives. For this purpose chloral hydrate and the nitrophenols were selected.

a. Chloral hydrate and gelatin

Weighed amounts of gelatin (1 g.) were immersed in aqueous solutions of chloral hydrate varying from 5 to 20 per cent. The strengths of the solu-

tions were estimated at the beginning of the experiment and then after standing at 15°C. for three days, by adding a known volume of N sodium hydroxide to a measured portion of the solution and titrating the excess of unused alkali with N sulfuric acid.



$$Cl_3C{\cdot}CH(OH)_2 + NaOH = CHCl_3 + HCOONa + H_2O$$

The results are given in table 1.

b. Chloral hydrate and egg albumin

Similar experiments were carried out with colloidal solutions of egg albumin. Ten cc. of water, in which 1 g. of the protein had been dissolved, were introduced into a series of viscose dialyzers, and these were then respectively immersed in solutions of chloral hydrate, varying from 0.[illegible] to 10 per cent in strength (50 cc.). By this means it was possible to ana[illegible]

TABLE 1

Chloral hydrate and gelatin

1 g. of gelatin to 60 cc. of chloral hydrate solution

WATER PHASE		WEIGHT OF CHLORAL HYDRATE TAKEN UP BY 1 G OF PROTEIN	DISTRIBUTION RATIO	CONDITION OF PROTEIN
Initial concentration per cc.	Final concentration per cc *A*	*B*	*B/A*	
grams	*grams*	*grams*		
0.1920	0.1853	0.402	2.1	Precipitated
0.1440	0.1407	0.198	1.4	
0.0960	0.0960	0	0	Unaffected
0.0480	0.0480	0	0	

the water phase in the complete absence of the protein phase after equilibrium had been attained (three days). The results are set out in table 2.

Parallel experiments were then set up with picric acid, the strengths of the aqueous solutions being estimated by titration with standard alkali (methyl red as indicator). Tables 3 and 4 give the results of these experiments.

The following conclusions may be drawn from these results. (1) In the case of chloral hydrate with gelatin there is a slightly increased value of the distribution ratio at precipitation, but with egg albumin no increase at all is apparent. (2) With picric acid, the distribution ratio also increases slightly when the precipitation of the gelatin first commences, but as the concentration of the picric acid rises, the ratio again falls rapidly in magnitude, although the protein remains permanently in the coagulated state.

The results are thus quite different from those observed in the case of phenol and cresol, and it may be concluded that the marked increase in the magnitude of the partition coefficient at precipitation observed with these substances is not general for all hydroxy compounds.

TABLE 2

Chloral hydrate and egg albumin

1 g. of albumin to 60 cc. of chloral hydrate solution

WATER PHASE		WEIGHT OF CHLORAL HYDRATE TAKEN UP BY 1 G. OF PROTEIN *B*	DISTRIBUTION RATIO *B/A*	CONDITION OF PROTEIN
Initial concentration per cc	Final concentration per cc. *A*			
grams	*grams*	*grams*		
0.0834	0.0810	0.1380	1.7	Precipitated
0 0331	0.0314	0.1020	3.2	Unaffected
0.0081	0.0079	0.0120	1 5	Unaffected
0 0041	0.0039	0 0120	3 0	Unaffected

TABLE 3

Gelatin and picric acid

0.5 g. of gelatin to 40 cc. of picric acid solution

WATER PHASE		WEIGHT OF PICRIC ACID TAKEN UP BY 1 G. OF PROTEIN *B*	DISTRIBUTION RATIO *B/A*	CONDITION OF PROTEIN
Initial concentration per cc	Final concentration per cc. *A*			
grams	*grams*	*grams*		
0 0112	0 0085	0.2154	25 3	Precipitated
0 0056	0 0033	0.1814	55.0	Precipitated
0 0028	0 0009	0.1527	158 5	Precipitated
0 0019	0.0005	0.1069	214 0	Precipitated
0.0011	0 0004	0 0534	133 5	Unaffected
0.0006	0.0004	0 0133	33 2	Unaffected

TABLE 4

Gelatin and edestin with phenol

CONDITION OF PROTEIN	WATER PHASE		AMOUNT OF PHENOL DISSOLVED BY 1 G. OF PROTEIN *B*	PARTITION COEFFICIENT *B/A*
	Initial concentration of phenol per cc.	Final concentration of phenol per cc. *A*		
(a) Gelatin. 1 g. of gelatin to 40 cc. of phenol solution				
	grams	*grams*	*grams*	
Precipitated by dialyzed iron	0.0023	0.0020	0 0124	6 2
"Sol"	0 0023	0.0021	0.0090	4.3
(b) Edestin. 1 g. of edestin to 40 cc. of phenol solution				
"Sol"	0.0032	0.0031	0.0040	1.3
Insoluble edestin chloride	0 0032	0.0031	0.0040	1.3

II. SOLVENT POWER OF COAGULATED PROTEINS FOR PHENOL

Experimental work has also been carried out with the object of ascertaining whether the increased solvent power for phenol, which is observed when proteins are coagulated by heat, or by the action of phenol itself, also takes place when precipitation of the protein is effected by other means.

In the first place, a comparison has been instituted between the solvent powers for phenol of a gelatin sol and gelatin precipitated by the addition of a colloid of opposite electric charge, e.g., dialyzed iron. And, in the second place a similar comparison has been made in the case of edestin dissolved in salt solution and the insoluble edestin chloride formed by adding a drop of hydrochloric acid to edestin solution.

a. Gelatin sols

Gelatin (1 g.) was introduced into viscose dialyzers, containing 15 cc. of a dilute phenol solution and immersed in 25 cc. of the same phenol solution. The experiment was carried out at 37°C., so that the gelatin dissolved and formed a "sol." Into one of the dialyzers sufficient dialyzed iron was added to precipitate the "sol," and after three days for equilibrium to be attained the phenol concentration in the protein-free water phase (outside the dialyzers) was estimated by Lloyd's method (3), which depends on the formation of tribromophenol from the interaction of bromine and phenol.

In the experiment with edestin 10 cc. of a 5 per cent salt solution in which 1 g. of the protein had been dissolved was introduced into dialyzers, which stood in 30 cc. of a phenol solution of known strength. To one of the dialyzers one drop of concentrated hydrochloric acid was added. After three days the phenol in the water phase was estimated as before.

The results of these experiments are shown in table 4. The observations show that in the case of gelatin the partition coefficient is slightly raised by precipitation with dialyzed iron, but the increase is small compared with that caused by precipitation of the gelatin by phenol itself (Cooper, 1912). In this case the partition coefficient rises as high as 30.

The results obtained in the edestin experiment indicate that the solvent power of an edestin "sol" for phenol is not increased at all by conversion into the precipitated chloride.

The increased solvent power is thus only manifested under certain experimental conditions, and is restricted to the particular cases of coagulation by heat and the action of phenols, i.e., it is associated strictly with the specific change induced in proteins by the process of "denaturation."

III. THE SIGNIFICANCE OF THE WATER FACTOR

Early in these researches (Cooper, 1923) it was realized that in a colloidal solution of a protein a portion of the water present is probably associated or imbibed with the protein phase, and this question was considered

in relation to the problems under investigation. Possibly the imbibed water might possess less marked solvent properties than normal water. Hence when the protein was dehydrated by coagulation, the associated water thrown out would dilute the water phase, and as a result the increased solvent power for phenol observed when a protein is coagulated might be merely apparent, and the calculations fictitious. Experiments carried out at the time, however, suggested that this was not the case, and the results supported the view that the calculated partition coefficients were real. Since then considerable progress has been made in the field of colloidal chemistry, and in view of the new data now available further experimental work has been carried out.

a. Experiments with red cells

According to Krevisky (2) the amount of free water in the red cell is equal to one-third of the cell volume, whilst an equal proportion of water is *bound* water, i.e., associated with the protein and hence forming part of the disperse phase.

By carrying out distribution experiments with red cells and phenol on the lines of those already described in this paper, it has therefore been possible to calculate the partition coefficients by two different methods: (1) assuming that the water imbibed in the protein phase is *normal* water and thus for purposes of calculation may be regarded as part of the water phase; (2) assuming that the association with the proteins renders the bound water abnormal in solvent properties and such that it must be regarded as an intimate constituent of the protein phase and not to be calculated as an integral part of the water phase.

Red cells were obtained by centrifuging ox and pig blood. Fifteen cubic centimeters were introduced into a series of viscose dialyzers, which were immersed in varying concentrations of phenol (25 cc.), and after three days for equilibrium the phenol solutions outside the dialyzers were again analyzed. The percentage of protein in red cells is 30 per cent.

The results have been calculated by the two different methods already mentioned, the respective data being as follows: (1) Protein 4.5 g. (30 per cent of red cells); water phase 25 cc. + 10 cc. (two-thirds of red cells) = 35 cc. (2) Protein 4.5 g.; water phase 25 cc. + 5 cc. (one-third of red cells) = 30 cc. (See tables 5A and 5B, respectively.)

b. Experiments with egg white

St. John (4) has shown that the amount of water bound with the proteins of egg white is equal to 20 per cent of the total water content.

Similar experiments to those carried out with red cells have therefore been made with egg white and phenol, and the partition coefficients have been calculated as before in two ways, (1) assuming the whole water content

TABLE 5A

Experiments with red cells

WATER PHASE		AMOUNT OF PHENOL DISSOLVED BY 1 G. OF PROTEINS	DISTRIBUTION RATIO
Initial phenol concentration per cc.	Final phenol concentration per cc. *A*	*B*	*B/A*
		Ox	
grams	*grams*	*grams*	
0.0043	0.0031	0.0093	3
0.0064	0.0040	0.0187	4.7
0.0071	0.0044	0.0209	4.7
0.0107	0.0074	0.0256	3.4
0.0150	0 0097	0.0412	4.2
0.0164	0.0103	0.0475	4.6
0.0236	0.0159	0 0599	3.6
0.0257	0.0162	0.0739	4.6
		Pig	
0.0088	0.0055	0.0256	4.6
0.0267	0.0178	0.0692	3.8
0.0381	0.0198	0.1423	7.2

TABLE 5B

Experiments with red cells

WATER PHASE		AMOUNT OF PHENOL DISSOLVED BY 1 G. OF PROTEINS	DISTRIBUTION RATIO
Initial phenol concentration per cc.	Final phenol concentration per cc. *A*	*B*	*B/A*
		Ox	
grams	*grams*	*grams*	
0.0050	0.0031	0.0126	4.1
0.0075	0.0040	0.0233	5.8
0.0083	0.0044	0.0260	5.9
0.0125	0.0074	0.0340	4.6
0.0175	0.0097	0.0520	5.4
0.0192	0.0103	0.0593	5.7
0.0275	0.0159	0.0773	4.8
0.0300	0.0162	0.0920	5.7
		Pig	
0.0103	0.0055	0.0320	5.8
0.0312	0.0178	0.0893	5.0
0.0445	0.0198	0.1646	8.3

of egg white is normal water and thus counted as water phase, and (2) assuming the bound water to be abnormal and thus regarded as part of the protein phase. Calculated in the ordinary way, the partition coefficients

$$\frac{\text{amount of phenol dissolved in protein sol}}{\text{amount of phenol dissolvod in water}}$$

were on the average 3.7. Calculated in the alternative way by regarding the proportion of bound water as a constituent of the disperse phase, the mean coefficient was 5.0. In the case of the coagulated protein, the partition coefficient was, however, 12.

From the experimental results with red cells and egg white it is seen that the particular method of calculation makes very little difference in the actual value of the distribution ratios. By introducing the correction for the amount of imbibed water, the distribution ratios only increase by about one-third. Yet the partition coefficient in the case of a coagulated protein is approximately four times as great as that for the protein in a state of colloidal solution. The increased solvent power for phenol noticed when a protein is coagulated is thus a reality, and is not due to fictitious calculations arising out of movements of water from one phase to the other.

A comparison was next made of the uptake of phenol by the moist and dry clot of egg white. Water is imbibed to a certain degree in a moist clot obtained by boiling a solution of egg white, but not by the clot after it has been dried at 100°C.

Thirty-five cubic centimeters of phenol solution were mixed with 10 cc. of half-strength egg white (i.e., egg white diluted with an equal volume of water and containing 6.0 per cent protein) for the moist clot experiment, the egg white then being coagulated in situ in the bottle by heat. For the dry clot experiment, 35 cc. of solution was used with 10 cc. of water and the *dried* and powdered clot from 10 cc. of diluted egg white was then added.

This experiment thus afforded a further simple method of studying the significance of the water factor.

WATER PHASE		AMOUNT OF PHENOL IN 1 G OF PROTEIN *B*	*B/A*
Initial concentration per cc.	Final concentration per cc. *A*		
grams	*grams*	*grams*	
0.01027	0 00729	0.2233	30.6 Moist clot
0.01027	0.00699	0.2460	35.2 Dry clot

The dry clot of egg white absorbs slightly more phenol than the moist clot from solutions of the same strength. Thus, in the case of phenol, it makes very little difference whether the water in the system is entirely in

one phase or whether it is present in the protein phase as well. The manner of distribution of the water hence does not affect the value of the partition coefficients to any appreciable extent, and the results are confirmatory of those already described in this section.

Although the rise in the value of the partition coefficient at coagulation is not due to errors in calculation introduced by transfer of water from one phase to another, yet this water factor may be of real significance in another way. The solubility of phenol in proteins will probably be diminished by the presence of bound or imbibed water, and the normal solvent power of proteins for phenol will hence not be manifested until the phenol replaces the associated water, which it will drive out through its dehydrating action, thus causing coagulation. According to this view the partition coefficients obtained with *coagulae* measure the *true* solubility of phenols in proteins, and an explanation is offered for the abnormally low coefficients observed with colloidal solutions.

The interpretation of the observations that the germicidal powers of phenol, cresol, and chlorophenols run parallel with their partition coefficients with *protein coagulae*, whilst the coefficients with protein sols are all of the same order of magnitude (about 3) is however not so clear. If the solubility of phenols in coagulae is regarded as their normal solubility in proteins, then germicidal power in the case of phenols is proportional to the *true* partition coefficients, and the formation of a *solution* of the disinfectant in the bacterial proteins may be considered the first stage in the process of disinfection. No explanation is then given, however, of the absence of proportionality between germicidal power and the partition coefficients measured with proteins in the natural state, in which they occur in the cell (sols and gels). At the present time it can only be suggested that the *bound* water diminishes the solubility of cresol and chlorophenol in proteins to a *greater* extent than it does that of phenol itself, thus tending to maintain the partition coefficients at approximately the same value in all cases. When, however, the protein becomes coagulated through the dehydrating effect of the phenols, the associated water is expelled and transferred to the continuous phase, and the *true* partition coefficient specific and characteristic of each individual phenol reveals itself. The first phase in the process of disinfection by phenols is thus the formation of a solution in the bacterial proteins followed by coagulation, and cresol and chlorophenol are superior to ordinary phenol in germicidal power, because they induce coagulation, i.e., expulsion of *bound* water, at a lower concentration (Cooper, 1913, 1923).

SUMMARY

1. Coagulated proteins possess a much higher solvent power for phenols than proteins in a natural condition, e.g., sols and gels. This is true also

of picric acid, but to a lesser degree. Chloral hydrate, however, is exceptional, the uptake of which by proteins is not materially affected by the physical state of the protein.

2. Proteins precipitated from colloidal solution by the addition of a colloid of opposite electric charge or by formation of an insoluble salt do not exhibit this increased solvent power for phenol.

3. By means of experiments with red cells and egg white, in which due allowance has been made for the proportion of water bound to the protein phase, it has been found that the increased partition coefficients observed at coagulation are realities, and not due to calculation errors introduced by movement of water from one phase to another. The imbibed water may however diminish the solubility of phenol in proteins, thus accounting in the case of sols and gels for the low partition coefficients, which rise to the normal figure when the water is expelled at coagulation.

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THE RATE OF SOLUTION OF MAGNESIUM IN ACIDS[1]

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In a preliminary paper (16) the authors have treated the problem of the rate of solution of magnesium in acids from the point of view of the extended theory of acids and bases (5, 18). The present paper is a continuation of that study with an attempt to consider the problem from the point of view of the diffusion rate theory as well as from that of the Brönsted-Kilpatrick theory. It will be demonstrated that in either case it is necessary to consider the extended theory of acids as an important factor.

Consider first the reactions which take place when magnesium reacts with a strong acid such as hydrogen chloride. When hydrogen chloride dissolves in water, we have

$$HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$$

and the reaction goes practically to completion to the right. The reaction can, therefore, involve the water, the hydrogen ion (H_3O^+), or the chloride ion. The metal itself is composed of magnesium ions (Mg^{++}) and free electrons (10).

Equation 1 gives one possible primary reaction.

$$H_3O^+ + e \rightarrow H_2O + H \tag{1}$$

This might be followed by the reactions

$$\underset{\text{(solid)}}{Mg^{++}} \rightleftarrows \underset{\text{(dissolved)}}{Mg^{++}} \tag{1a}$$

$$2H \rightarrow H_2 \tag{1b}$$

the hydrogen escaping in the gaseous state. It is also possible for the primary reaction (3) to be

$$\underset{\text{(solid)}}{Mg^{++}} + Cl^- \rightarrow MgCl^+ \text{ or } MgCl_2 \tag{2}$$

which would be followed by reactions 1 and 1b.

[1] Abstracted from the thesis of John Henry Rushton presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, April, 1933.

Centnerszwer (8) considers the reaction to be between the metal and the molecular acid, but his computations are based upon the application of the classical law of mass action to solutions of strong electrolytes and cannot be accepted (14).

If equation 1 is accepted as more probable, then in accordance with the extended theory of acids, any proton carrier should react with the metal, and for weak acids there should be a reaction with the molecules, as well as with the hydrogen ions. For example, in the case of acetic acid,

$$CH_3COOH + H_2O \rightleftarrows H_3O^+ + CH_3COO^-$$

and since this reaction does not go to completion to the right, in addition to the water reaction, two reactions are possible

$$H_3O^+ + e \rightarrow H_2O + H \qquad (1)$$
$$CH_3COOH + e \rightarrow CH_3COO^- + H \qquad (3)$$

In fact, in accordance with the formal definition of an acid,

$$\begin{array}{ccccc} \text{Acid} & \leftrightarrows & \text{Base} & + & \text{Proton} \\ A & \rightleftarrows & B & + & H^+ \end{array} \qquad (4)$$

Where A represents an acid and B its conjugate base, we have the general double acid–base reaction (6),

$$\begin{array}{ccccccc} A & + & e & \rightarrow & B & + & A \\ \text{Acid 1} & & \text{Base 2} & & \text{Base 1} & & \text{Acid 2} \end{array} \qquad (5)$$

where A can be H_3O^+, CH_3COOH, $CH_2ClCOOH$, $C_5H_5NH^+$, H_2O, etc. The water reaction is readily detectable at higher temperature as will be shown later.

The question of which is the rate-controlling process has been discussed recently by Hammett (11) in connection with the work of Brönsted and Kane on sodium amalgams. Hammett concludes that if it could be proved that diffusion was not a factor in the determination of the reaction velocity in the experiments of Brönsted and Kane and of Kilpatrick and Rushton, these experiments would be strong evidence for reaction 1 as the rate-determining step. King and Braverman (17) conclude that while the "old diffusion theory" is not satisfactory without modification, certain results are definitely contradictory to the Brönsted-Kilpatrick theory. King and Braverman are vague as to the modification. In explanation of the dissolution of metals, Palmaer (20) accepts the theory of local elements of de la Rive (9), and definitely rejects the diffusion theory. The theory of local elements seems to be well founded for impure metals, but does not apply to pure magnesium.

In the first experimental section the dissolving of magnesium in strong acids will be described. The temperature coefficient of the reaction, the

relation of the rate to the concentration and volume of the solution and to the surface of the metal, the effect of stirring, and the effect of viscosity will be discussed.

EXPERIMENTAL PART

Four separate methods were used to follow the reaction. The amount reacted was determined at definite intervals of time by first, weighing the metal, second, measuring the volume of hydrogen evolved, third, titrating the solution, or fourth, measuring the amount of acid required to maintain a definite hydrogen-ion concentration as shown by an indicator. The last method was used in the study of the water reaction.

The apparatus used differed for the several methods mentioned above for following the reaction. The majority of the experiments were followed by measurement of the volume of hydrogen evolved. Samples of gas given off in reactions with hydrochloric, acetic, chloroacetic, and formic acids were analyzed for gases other than hydrogen. Hydrogen was found to be the only gas evolved. Two types of apparatus were employed, one for experiments at 0° and 25°C., and another for experiments at higher temperatures. Figure 1 illustrates the apparatus used in the 25°C. thermostat. Figure 2 shows the apparatus used for work at temperatures higher than 25°C.

The reaction chamber of these two pieces of apparatus differed both in size and shape. The 25°C. reaction flask was either a 300-cc. Florence flask or a special cylindrical flask as shown in the diagram. This special flask was used so that the level of the solution could be adjusted to various sizes of metal bars. The reaction vessel in the vapor thermostat was cylindrical and of very much smaller capacity. Several runs were made in the vapor thermostat by passing water at 25°C. through the vapor chamber of the thermostat. In this way parallel experiments were made in the two distinctly different reaction vessels and the results checked with each other. In each of the two pieces of apparatus the gas given off during the reaction was led to a water-jacketed gas buret, where the volume could be read at atmospheric pressure.

In the vapor thermostat the metal bar was first placed in the reaction vessel and allowed to come to temperature while a solution was placed in the delivery tube. Upon reaching thermal equilibrium, stopcock A was set so that when stopcocks B and C were opened the solution drained into the reaction vessel and the total volume of the system remained unchanged. Stopcock A was then turned so that the gas was delivered to the buret. As soon as the pressure in the gas buret could be made equal to atmospheric pressure, stopcock C was closed. By this method no gas was lost at any part of the reaction. Various liquids were used for work at the different temperatures.

Any part of the cylindrical bar of magnesium above the solution, or where reaction was not desired, was covered with collodion. No special

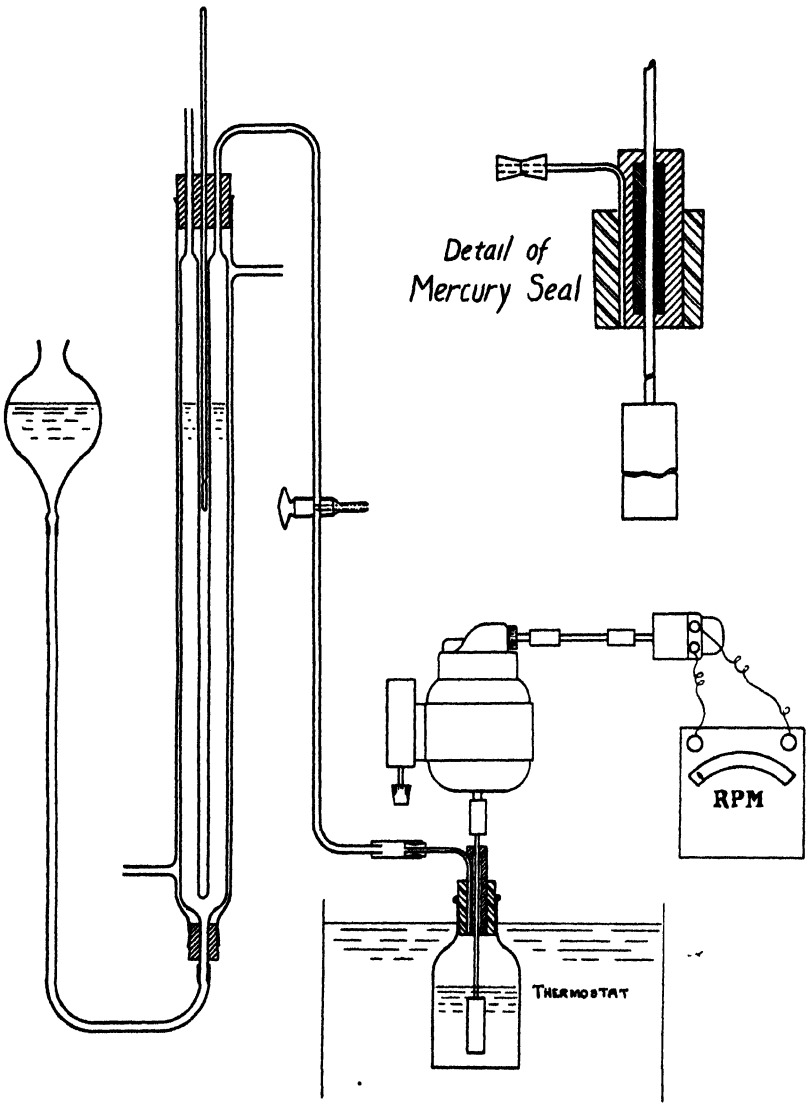

FIG. 1. APPARATUS FOR EXPERIMENTS AT 25°C. AND AT 0°C.

methods were used to make the metallic surface active. It was found unnecessary to do this in the case of magnesium. The surface of the metal exposed varied from 7 to 35 cm.^{2} The metal cylinder was held in

solution by a small steel rod threaded into one end of the bar. The steel rod was passed through a steel cap containing mercury, forming a seal (see detail in figure 1) (13). The end of the steel rod was attached directly to an electric motor whose speed could be controlled by a small resistance.

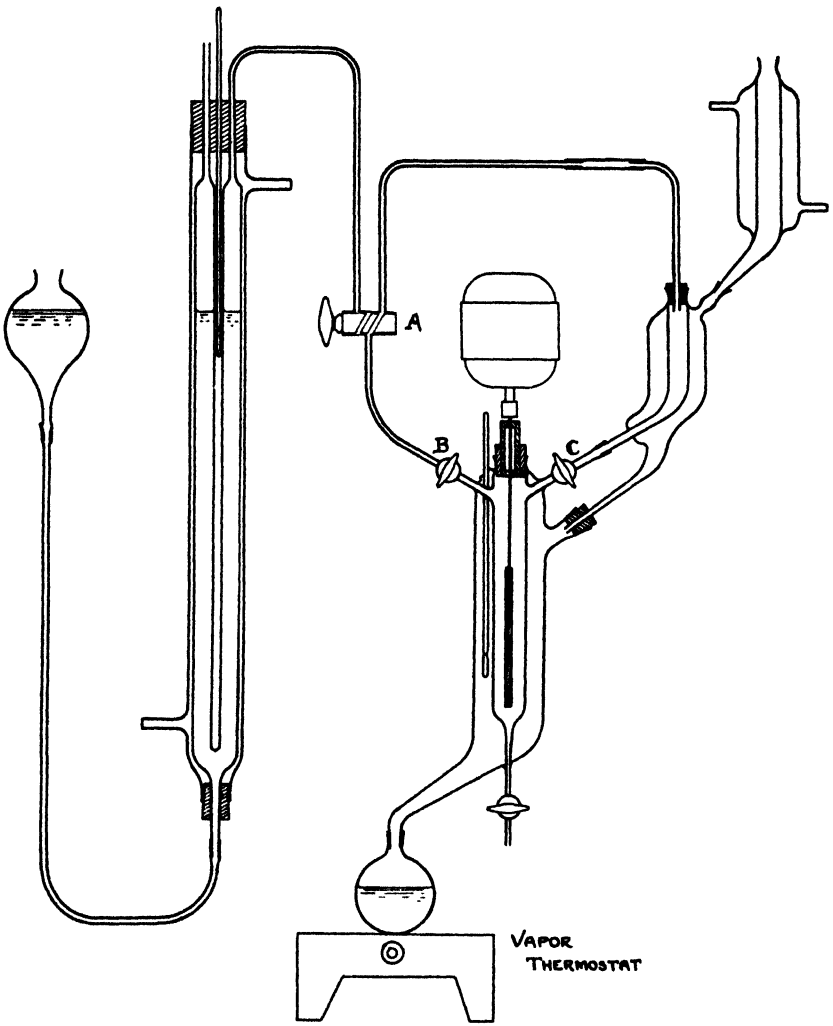

FIG. 2. APPARATUS FOR EXPERIMENTS AT ELEVATED TEMPERATURES

The opposite end of the motor shaft was connected to an electric tachometer with a scale reading directly in revolutions per minute.

To measure the rate of reaction by weight determinations, a set of stirrers was built. Six shafts were run simultaneously from a main shaft driven by an electric motor whose speed was controlled by a rheostat. Bars of

metal were threaded onto the Bakelite shafts coupled to the main shaft. Six experiments were run simultaneously, the bars washed, dried, and weighed. Other weight determinations were made using the apparatus shown in figure 1.

TABLE 1

Data for two hydrochloric acid experiments

TIME	NUMBER 5*			NUMBER 22†		
	Hydrogen evolved H_t	$H_0 - H_t$	Log $\frac{H_0}{H_0 - H_t}$	Hydrogen evolved H_t	$H_0 - H_t$	Log $\frac{H_0}{H_0 - H_t}$
minutes	*cc.*			*cc.*		
1	6.0	132.2	0.0200	4.35	63.65	0.0285
2	11.4	126.8	0.0380	8.50	59.50	0.0570
3	16.8	121.4	0.0565	12.20	55.80	0.0855
4	22.0	116.2	0.0755	15.75	52.25	0 1140
5	26.6	111.6	0.9038	19.05	48.95	0.1425
6	31.5	106.7	0.1130	22.05	45 95	0.1710
7	36.0	102.2	0.1313	25.10	42.90	0 1995
8	40.3	97.9	0.1500	27.80	40.20	0.2280
9	44.4	93.8	0.1532	30.35	37.65	0.2565
10	48.4	89.8	0.1875	32.75	35.25	0.2850
11	52.2	86.0	0.2062	35.00	33.00	0.3135
12	55.8	82.4	0.2250	37.10	30 90	0.3320
13	59.2	79.0	0.2435	39.05	28.95	0.3705
14	62.6	75.6	0.2622	40.90	27.1	0.3990
15	65.7	72.5	0.2808	42.60	25.4	0.4275
16	68.8	69.4	0.2995	44.25	23.75	0.4570
17	71.7	66.5	0.3180	45.75	22.25	0 4850
18	74.5	63.7	0.3370	47.175	20.825	0.5125
19	77.2	61.0	0.3558	48.48	19.52	0 542
20	79.8	58.4	0.3743	49.70	18 3	0.570

* Experiment No. 5. Temperature = 25°C.; initial concentration of acid = 0.050 M; volume of acid = 225 cc.; H_0 = 138.2 cc.; surface speed = 2150 cm. per minute; metal area = 7.01 cm.^{2}; 57.8 per cent of reaction followed; no sodium chloride present; k at 2000 cm. per minute = 1.36.

† Experiment No. 22. Temperature = 25°C.; initial concentration of acid = 0.025 M; volume of acid = 225 cc.; H_0 = 68.0 cc.; surface speed = 2670 cm. per minute; metal area = 10.39 cm.^{2}; 65.3 per cent of reaction followed; 0.025 M sodium chloride present; k at 2000 cm. per minute = 1.34.

Experiments in the various reaction vessels showed that the rate of reaction as measured by the volume of hydrogen evolved, by the weight of metal dissolved, and by the decrease in acid concentration were in agreement. The shape of the reaction vessel and the length and diameter of the metal cylinder had no effect. The magnesium[2] itself was for most experiments

[2] For this magnesium, the authors wish to thank The Aluminum Company of America.

of very high purity. The analysis showed no copper, zinc, lead, or free iron, 0.18 per cent of magnesium oxide, 0.02 per cent of silicon, and 0.02 per cent of iron and aluminum. A few experiments made with ordinary C.P. magnesium sticks gave no appreciable difference in rate.

METHODS OF EXPRESSING RESULTS

The kinetic equation, based on the hypothesis that the rate depends on the collisions of the acid with the metal and is consequently proportional

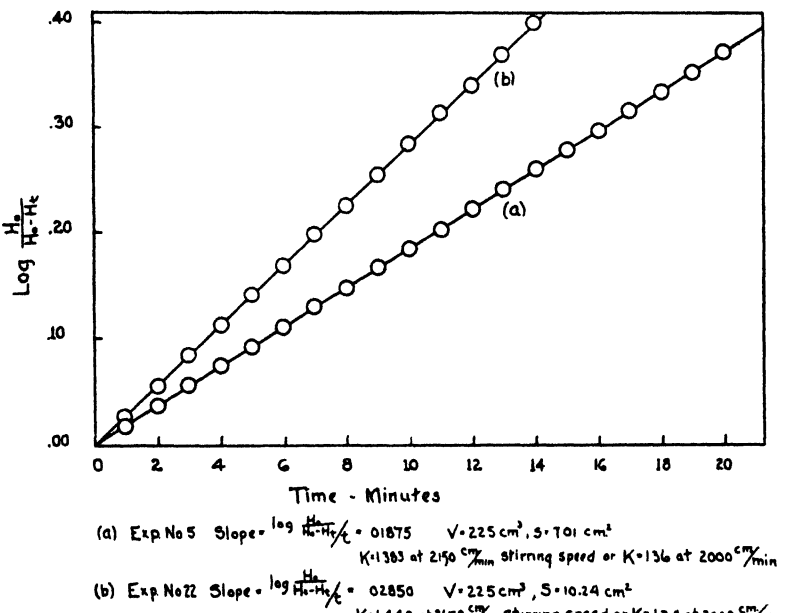

FIG. 3. RELATION BETWEEN $\log \frac{H_0}{H_0 - H_t}$ AND TIME FOR HYDROCHLORIC ACID EXPERIMENTS NOS. 5 AND 22

to the acid concentration and to the surface of the metal, yields for the velocity constant of the reaction

$$k = \frac{2.3V}{St} \log \frac{C_0}{C_t} \tag{6}$$

where V is the volume of the solution, S the surface, t the time, C_0 the initial acid concentration, and C_t the concentration at time t.

The same expression can be derived by assuming that the rate is controlled by a process of diffusion, and employing Fick's law. Consequently the fact that equation 6 fits the data does not distinguish between a chemical process and a process controlled by diffusion. Throughout the paper

V is expressed in cm.^{3}, S in cm.^{2}, and t in minutes, so that k has the dimension cm. $\times$ min.$^{-1}$.

Table 1 gives the necessary data for two typical experiments with hydrochloric acid. Figure 3, in which $\log \frac{H_0}{H_0 - H_t}$ is plotted as ordinate and

TABLE 2

Experiments at 25°C.

Stirring speed = 2000 cm. per minute. Volume of solution = 225 cc.

EXPERIMENT NO.	AREA OF METAL SURFACE S	k_1
5	7.01	0.04235
4	7.38	0.0403
23	10.38	0.0604
22	10.39	0.0618
3	7.71	0.0456
18	13.64	0.0807
17	13.65	0.0813
13	13.81	0.0786
14	13.78	0.0815
20	10.42	0.0635
19	10.43	0.0635
59	25.38	0.1530
25	32.42	0.1917
26	32.35	0.1925
24	32.40	0.193

TABLE 3

Experiments at 25°C.

Stirring speed = 2000 cm. per minute. Unit surface area

NUMBER OF DUPLICATE EXPERIMENTS	VOLUME OF ACID V	$\frac{1}{V}$	AVERAGE VALUE OF k_2	DEVIATION OF k_2
	cc.			*per cent*
5	37.5	0.02665	0.03575	4.2
3	180.0	0.05550	0.00745	1.9
5	215.0	0.00465	0.00624	0.5
5	225.0	0.00445	0.00595	2.1

time as abscissa, shows that the reaction follows the pseudo monomolecular law. The slope of the line is $\frac{k_1}{2.3}$, where

$$k_1 = \frac{2.3}{t} \log \frac{H_0}{H_0 - H_t} \tag{7}$$

k_1 may be calculated for a series of solutions, using different volumes of solution and different areas of surface.

EFFECT OF SURFACE

Table 2 gives the k_1 values for a number of experiments in which the same volume of solution was used and the area of the surface of the metal was varied. The values of k_1 are shown in relation to the surface in figure 4. Over a wide range of surface k_1 is inversely proportional to the surface.

A constant k_2 may now be defined

$$k_2 = \frac{k_1}{S} \quad \text{or} \quad k_2 = \frac{2.3}{St} \log \frac{H_0}{H_0 - H_t} \tag{8}$$

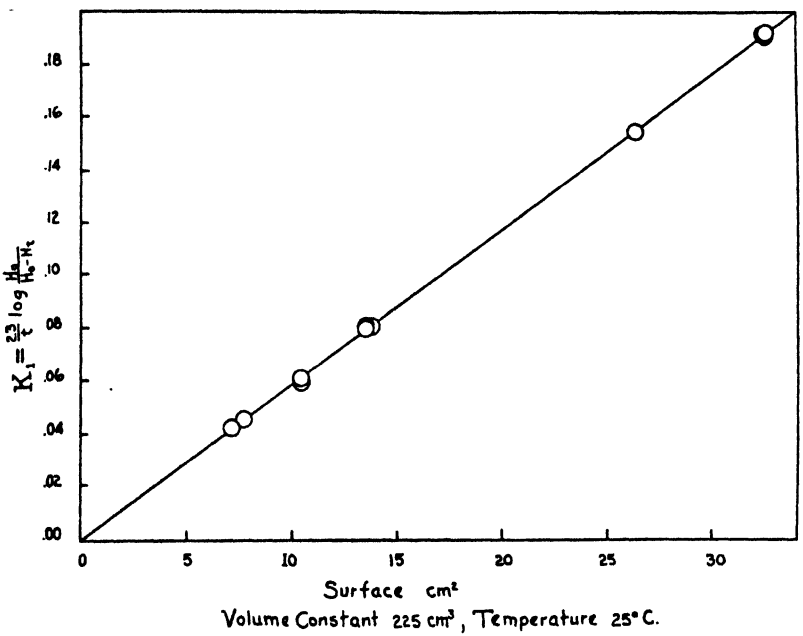

FIG. 4. RELATION BETWEEN k_1 AND SURFACE

The values of k_2 are given for varying volumes of solution in table 3 and show that

$$k = k_2 V \quad \text{or} \quad k = \frac{2.3V}{St} \log \frac{H_0}{H_0 - H_t} \tag{6}$$

These relations have been determined for solutions having the same constant stirring. Table 4 gives the data used to relate k to the stirring of the solution. It was found that different amounts of stirring resulted with cylinders of metal of different diameters, and in order to measure stirring

TABLE 4

Hydrochloric acid experiments at 25°C.

EXPERIMENT NO.	SPEED OF METAL BAR	SURFACE STIRRING SPEED	k AT EXPERIMENT SPEED	k AT 2000 CM. PER MINUTE STIRRING SPEED	PER CENT OF REACTION FOLLOWED	INITIAL CONCENTRATION OF ACID
	r.p.m.	*cm. per min.*				*moles per liter*
33	0	0	0.235		10.7	0.050
34	0	0	0.232		27.0	0.050
35	0	0	0.231		30.8	0.050
36	0	0	0.225		41.2	0.050
37	0	0	0.229		56.0	0.050
7	600	1550	1.418	1.51	62.4	0.050
6	600	1590	1.504	1.61	59.8	0.025
8	800	2000	1.46	1.46	62.3	0.051
5	800	2150	1.38	1.36	57.8	0.050
4	800	2170	1.245	1.23	41.1	0.075
9	900	2200	1.495	1.46	62.3	0.050
23	800	2650	1.403	1.31	12.0	0.1235
22	800	2670	1.442	1.34	65.3	0.025
21	800	2700	1.31	1.20	12.5	0.075
3	1000	2730	1.44	1.33	39.0	0 1235
1	1000	2940	0.932	0.83	82 5	0.012
2	1000	2940	0.932	0.83	82.5	0.012
18	800	3060	1 485	1.33	66.5	0.050
17	800	3080	1.502	1.34	66.7	0 050
10	850	3090	1.268	1.08	61.2	0.050
13	1200	4700	1.695	1.28	61.8	0.050
14	1200	4500	1.690	1.33	64.4	0 050
38	2210	5570	1.30	0.97	99.2	0.010
59	2250	5840	1.68	1.22	99.5	0 050
53	2550	6240	1.87	1.34	100.	0.050
51	2550	6270	1.87	1 35	100.	0 050
52	2550	6240	1.70	1.22	99 3	0.025
50	2550	6270	1.78	1.28	98.0	0 025
49	2550	6300	1.78	1.34	98.0	0 025
48	2550	6300	1.94	1.38	98.5	0.050
47	2550	6300	1.99	1.42	98.7	0.050
46	2550	6320	1.78	1.28	100.	0.050
45	2550	6320	2.00	1.41	98.7	0.050
11	1850	7330	1.99	1.37	11.6	0.050
16	1850	7350	1.98	1.37	11.4	0.050
20	2800	9520	2.15	1.37	9.5	0.050
25	2000	9550	2.080	1.33	100.	0.050
19	2800	9580	2.162	1.37	1.0	0.050
26	2000	9670	2.125	1.34	100.	0.050
24	2000	9740	2.100	1.34	100.	0.050
15	3100	11800	2.472	1.47	1.5	0.050
12	3100	12200	2.460	1.46	1.5	0.050
				Av. = 1.33		

the surface velocity R was employed by multiplying the circumference of the cylinder by the revolutions per minute.

When the logarithm of the surface speed was plotted against the corresponding logarithm of k, it was found that the following relation held over a wide range of surface speeds,

$$k = aR^n \tag{9}$$

where a and n are constants, n being the slope of the line in figure 5 and a

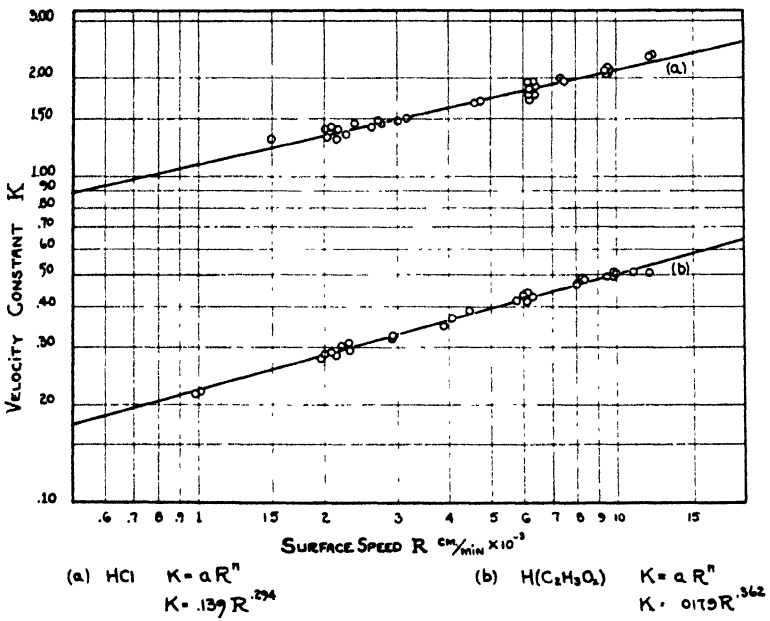

FIG. 5. LOGARITHMIC RELATION BETWEEN k AND STIRRING SPEED

TABLE 5

Hydrochloric acid experiments at 25°C.

NUMBER OF DUPLICATE EXPERIMENTS	METHOD	AVERAGE VALUES OF k AT 2000 CM PER MINUTE STIRRING	AVERAGE DEVIATION
			per cent
8	Weight	1.309	8.5
35	Volume	1.335	6 0
8	Titration	1.312	7 2

the value of k when $R = 1$. The values of a and n for magnesium and hydrochloric acid are 0.139 and 0.362, respectively.

Acetic acid behaves in a similar way, the essential difference being the value of a in equation 9. Many experiments were performed at surface speeds in the neighborhood of 2000 cm. per minute. To make all experi-

ments comparable, the values of k have been calculated to 2000 cm. per minute by equation 9 and are given in table 5. The maximum deviation

TABLE 6

Values for hydrochloric acid experiments at 25°C.

All rate data at stirring speed of 2000 cm. per minute

NUMBER OF DUPLICATE EXPERIMENTS	CONCENTRATION OF ACID	AVERAGE MILLIEQUIVALENTS REACTED PER LITER PER CM.² PER MINUTE OVER 1/10 REACTION	AVERAGE DEVIATION
	M		*per cent*
4	0.010	0.01062	7.2
2	0.012	0.00966	9.4
10	0.025	0.03246	5.7
25	0.050	0.06405	6.5
6	0.075	0.08605	6.6
4	0.1235	0.15440	7.3

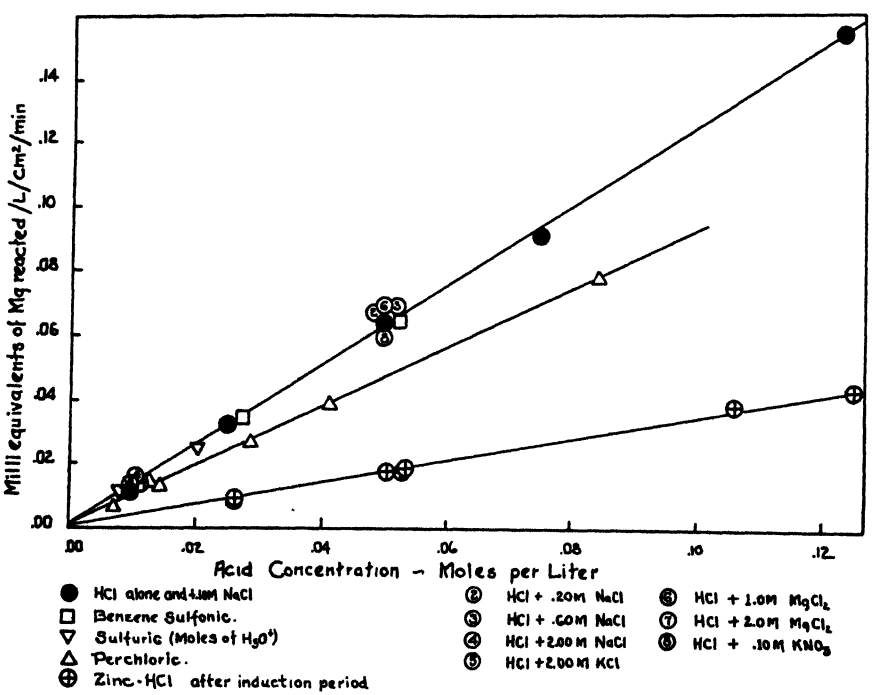

FIG. 6. REACTION WITH THE ACID H_3O^+

in k_{2000} is 17.5 per cent, and the average deviation is 6.1 per cent. These values include the earlier experiments where the rate of stirring was not

determined accurately. Table 5 gives the values of k obtained by gas volume, by measurements of loss in weight of magnesium, and by titration of the solution. All the methods agree with the experimental error.

RELATION TO HYDROGEN-ION CONCENTRATION FOR STRONG ACIDS

In order to show the proportionality between the rate of reaction and the hydrogen-ion (H_3O^+) concentration, the one-tenth time of reaction was calculated from k and the average milliequivalents of magnesium reacted per minute, per square centimeter of surface, per liter of solution, at a stirring speed of 2000 cm. per minute. Table 6 gives these results and figure 6 shows the proportionality of the rate to the hydrogen-ion

TABLE 7

Values for hydrochloric acid experiments at 25°C.

NUMBER OF DUPLICATE EXPERIMENTS	SALT ADDED	RATIO OF SALT TO ACID	VISCOSITY RELATIVE TO WATER	k_{2000}	DEVIATION FROM THE AVERAGE k_{2000}
					per cent
8	None	0	1.004	1 30	2 3
11	0.1 *M* NaCl	1 to 1	1 008	1.32	0.7
19	0.1 *M* NaCl	2 to 1	1 009	1.35	1.5
1	0 1 *M* NaCl	4 to 1	1 020	1.51	13 5
1	0 6 *M* NaCl	12 to 1	1 050	1.46	9 8
2	2.0 *M* NaCl	20 to 1	1.205	1.49	12 0
2	0.1 *M* KCl	2 to 1	0 999	1.365	2 6
2	2.0 *M* KCl	20 to 1	1.002	1.47	10 5
1	1.0 *M* $MgCl_2$	20 to 1	1.468	1.45	9 0
2	2.0 *M* $MgCl_2$	20 to 1	2.233	1.01	24 0
2	0.1 *M* KNO_3	2 to 1	0 995	1.22	8 3

concentration. The intercept on the milliequivalent axis represents the water reaction, which will be discussed in a later section.

EFFECT OF ADDED SALTS AND NON-ELECTROLYTES

In table 7 data are presented showing the change in k upon the addition of salts. In the fourth column is given the viscosity relative to water and in the sixth column is given the percentage change from k_{2000} for hydrochloric acid alone. In the case of 2 *M* sodium chloride the viscosity is 19.4 per cent higher than for 0.1 *M* sodium chloride, whereas k is 9.0 per cent higher. A 2 *M* potassium chloride solution has the same viscosity as a 0.1 *M* sodium chloride solution, but k is 9 per cent higher. Furthermore a 2 *M* magnesium chloride solution has a viscosity 200 per cent higher than a 0.1 *M* sodium chloride solution, but k is 25.2 per cent lower. From this it would appear that for these salts there is no general relation between rate of solution and viscosity.

In the case of non-electrolytes there seems to be a qualitative relationship, as shown in table 8.

TABLE 8

Values for viscosity experiments

NUMBER OF DUPLICATE EXPERIMENTS	SUGAR	GLYCERINE	VISCOSITY	RELATIVE VISCOSITY WATER TO SOLUTION	k_{2000}	DECREASE FROM AVERAGE k_{2000}	VISCOSITY INCREASE
(a) Values for 0.05 *M* hydrochloric acid experiments with sugar at 25°C.							
	moles per liter	*moles per liter*	*millipoises*			*per cent*	*per cent*
25	0		9 0	0.993	1 33	0	0
4	0.137		9.5	0 942	0.988	25.6	5.6
2	0.257		11.1	0 805	0.674	49.6	23.4
4	0 439		14 3	0 625	0 205	84.3	59 0
(b) Values for 0.05 *M* acetic acid experiments with sugar at 25°C.							
25	0		9 0	0.993	0 284	0	0
4	0 137		9 5	0.942	0 260	8.5	5.6
2	0.257		11 1	0.805	0 167	41.2	23.4
2	0.439		14 3	0 625	0 0546	80.6	59 0
(c) Values for 0.05 *M* acetic acid experiments with glycerine at 25°C.							
25		0	9.0	0.993	0.284	0	0
2		0.608	10.9	0.820	0.234	17.6	21 1
2		1.087	12 0	0.745	0.154	45.8	33 2
3		1.900	15 0	0.596	0 049	82.7	66.6

TABLE 9

Summary of variations of k with temperature

NUMBER OF DUPLICATE EXPERIMENTS	TEMPERATURE	$\frac{1}{T} \times 10^4$	AVERAGE k_{2000}	LOG k_{2000}	HEAT OF ACTIVATION	
	degrees C.					
2	0	36.6	0 444	−0.3526	k_{25}/k_0	7,120
38	25.0	33.5	1.338	+0.1260		
2	56.5	30.3	8.55	0.9320	$k_{56.5}/k_{25}$	11,500
2	76.0	28.65	22.20	1.3464	k_{76}/k_{25}	11,380
11	80.2	28.3	21.25	1.3274	k_{80}/k_{25}	10,520

EFFECT OF TEMPERATURE

The results of the determinations at different temperatures are given in table 9, and for the dissolution of magnesium in hydrochloric acid the logarithm of k is plotted against $1/T$ in figure 7. According to the Arrhenius equation, the slope of the line in figure 7 is $-\frac{A}{4.574}$, which gives a heat

of activation of 10,200 calories. This corresponds to a temperature coefficient $k_{35}/k_{25} = 1.75$. A discussion of this value in relation to the diffusion theory will be given later.

EXPERIMENTS WITH OTHER STRONG ACIDS

Since in the case of strong acids H_3O^+ is the only acid present besides water, one would expect that all strong acids would give the same velocity

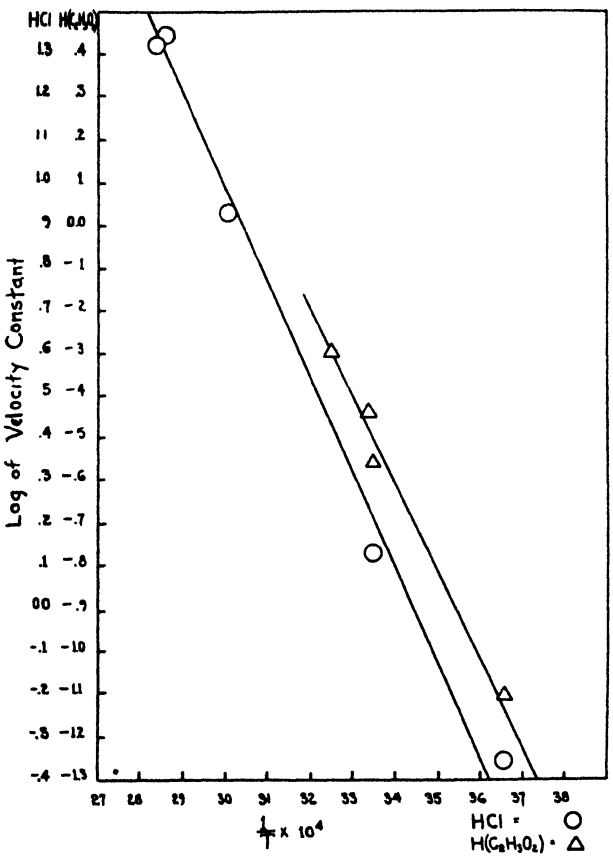

FIG. 7. RELATION BETWEEN VELOCITY CONSTANT AND TEMPERATURE

constant except for changes due to primary salt effect if the rate is a chemical one, or changes due to viscosity if the rate is controlled by a diffusion process. Table 10 gives the results for perchloric acid and benzenesulfonic acid, and the proportionality to the hydrogen-ion concentration is shown in figure 6.

Perchloric acid gives lower values of k than benzenesulfonic or hydrochloric acids. In the case of sulfuric acid the concentrations of the hydro-

gen ion and the HSO_4^- ion were calculated from known values of the classical dissociation constant at the proper ionic strengths, and $k_{H_3O^+}$

TABLE 10

Data for perchloric acid and benzenesulfonic acid at 25°C.

CONCENTRATION OF ACID	SODIUM CHLORIDE CONCENTRATION	k_{2000}	DEVIATION FROM AVERAGE k_{2000}	MILLIEQUIVALENTS PER LITER PER CM.² PER MINUTE	PER CENT OF REACTION FOLLOWED
(a) Perchloric acid					
moles per liter	*moles per liter*		*per cent*		
0.0073	0	0.919	14.0	0.00635	63
0.0141	0	1.016	6.1	0.01355	63
0.0293	0	0.980	8.4	0.0272	39
0.0417	0	1.003	6.2	0.0397	59
0.0835	0	0.997	6.8	0.0790	78
0.0123	0.10	1.215	13.0	0.0142	95
(b) Benzenesulfonic acid					
0.025	0.10	1.320	0.7	0.0313	56
0.050	0.10	1.340	0.7	0.0634	46

TABLE 11

Summary of data for sulfuric acid and bisulfate ion at 25°C.

CONCENTRATION OF ACID	CONCENTRATION OF NaCl	k_{2000}	DEVIATION FROM AVERAGE k_{2000}	MILLIEQUIVALENTS PER LITER PER CM.² PER MINUTE	PER CENT OF REACTION FOLLOWED
(a) Sulfuric acid					
M	*M*		*per cent*		
0.00926	0.10	1.407	9.5	0.0124	88.3
0.00926	0.10	1.322	2.9	0.0116	86 7
0.0184	0.10	1.182	7.9	0.0207	93 2
0.0184	0.10	1.227	4.5	0.0215	93.9
(b) Bisulfate ion (1 HSO_4^- to 1 Na_2SO_4)					
0.00139	0.0875	0.534	2.7	0.00071	82.6
0.00139	0.0875	0.534	2.7	0.00071	96 3
0.0040	0.075	0.525	1.1	0.00195	95.7
0.0040	0.075	0.525	1.1	0.00195	90.2
0.00761	0.0625	0.494	5.0	0.00358	89.5
0.00761	0.0625	0.508	2.2	0.00367	94.4
0.0109	0	0.535	3.0	0.00555	96.5
0.0109	0	0.500	3.8	0.00518	94.8

and $k_{HSO_4^-}$ calculated from the kinetic measurements. The results are given in table 11. It is seen that $k_{H_3O^+}$ is the same as that from hydrochloric and benzenesulfonic acids, while $k_{HSO_4^-}$ is decidedly less. The

results for sulfuric acid are presented in figure 6, while those for the HSO_4^- ion are given graphically in figure 14. In reducing all experiments to 2000 cm. per minute in surface speed, it has been assumed that the relation for all strong acids is the same as that found for aqueous hydrogen chloride.

THE WATER REACTION

Magnesium reacts readily with water at higher temperatures and, as will be shown, this reaction is independent of the hydrogen-ion concentration.

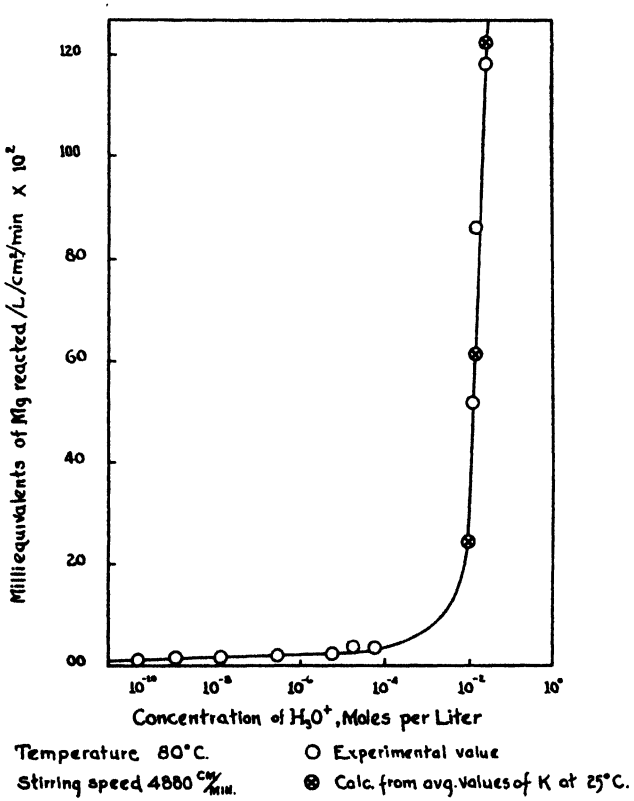

FIG. 8. MILLIEQUIVALENTS VERSUS CONCENTRATION H_3O^+

As the concentration of the water is constant, the velocity can be expressed by the equation

$$v = k_w + k_{H_3O^+}C_{H_3O^+} \tag{10}$$

when there are no other acids present. k_w represents the water reaction.

That k_w is independent of the hydrogen-ion concentration was demonstrated experimentally by using the fourth method. The method consisted in maintaining a constant hydrogen-ion concentration by adding small

amounts of strong acid from a microburet in the presence of an indicator. The amount of acid required was recorded at suitable intervals of time. It was found that acid was consumed at a constant rate.

The apparatus shown in figure 2 was used, without the gas buret. Experiments were carried out at the boiling point of benzene and of acetone. In table 12 are presented the results with and without added salt.

TABLE 12

Data for the water reaction

Stirring surface speed = 4880 cm. per minute

(a) Water at 80° and 56.5°C.

INDICATOR	CONCENTRATION OF H_3O^+	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE $\times 10^{-2}$ AT 80°C	MILLIEQUIVALENTS $\times 10^{-2}$ AT 56.5°C	HEAT OF ACTIVATION A	TEMPERATURE COEFFICIENT $\frac{k_{80.5}}{k_{56.5}}$
				calories	
Phenolphthalein	2×10^{-10}	1.088	0.991	930	1.04
Thymol blue	1.3×10^{-9}	1.288	0.688	6130	1.30
Phenol red	1.6×10^{-8}	1.672	0.799	7250	1.36
Bromcresol purple	5×10^{-7}	1.782	0.881	7030	1.34
Methyl red	8×10^{-6}	2.365	1.232	6420	1.31
Bromcresol green	3×10^{-5}	3.775	1.859	6990	1.34
Bromphenol blue	8×10^{-5}	3.560	1.628	7670	1.38
Thymol blue	2×10^{-2}	51.50	26.8	6550	1.32

(b) Solutions of magnesium chloride at 80°C.

CONCENTRATION OF H_3O^+	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE $\times 10^{-2}$ FOR 0.1 M $MgCl_2$	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE $\times 10^{-2}$ FOR 0.05 M $MgCl_2$	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE $\times 10^{-2}$ FOR 0.05 M KNO_3	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE $\times 10^{-2}$ FOR 0.10 M KNO_3
2×10^{-10}	3.74	2.32	2.30	
1.3×10^{-9}	3.24			
1.6×10^{-8}	3.63			
5×10^{-7}	3.52	2.22	2.36	3.64
8×10^{-6}	4.64			
3×10^{-5}	6.69			
8×10^{-5}	7.95	5.54	3.50	7.82

The results without added salt are presented graphically in figure 8. Included in this figure are points obtained by the second method for experiments at low concentrations of acid, the milliequivalents reacted per minute being corrected to the same surface speed. These points are in excellent agreement with those obtained by the fourth method. Figure 8 shows that below a hydrogen-ion concentration of $1 \times 10^{-5}M$ the reaction due to the

hydrogen ion is negligible, and the rate is independent of the hydrogen-ion concentration. The curve of figure 8 is quite similar to certain cases observed in homogeneous catalysis (23). It is to be noted that the temperature coefficient $\frac{k_{60.5}}{k_{56.5}}$ is 1.34, which corresponds to a heat of activation of 7000 calories as against 10,000 for the H_3O^+ reaction.

The effect of salts was also studied; these results are given in table 12 and figure 9. In the experiments with added salt no allowance was made for the change in the dissociation constant of the indicator with change in

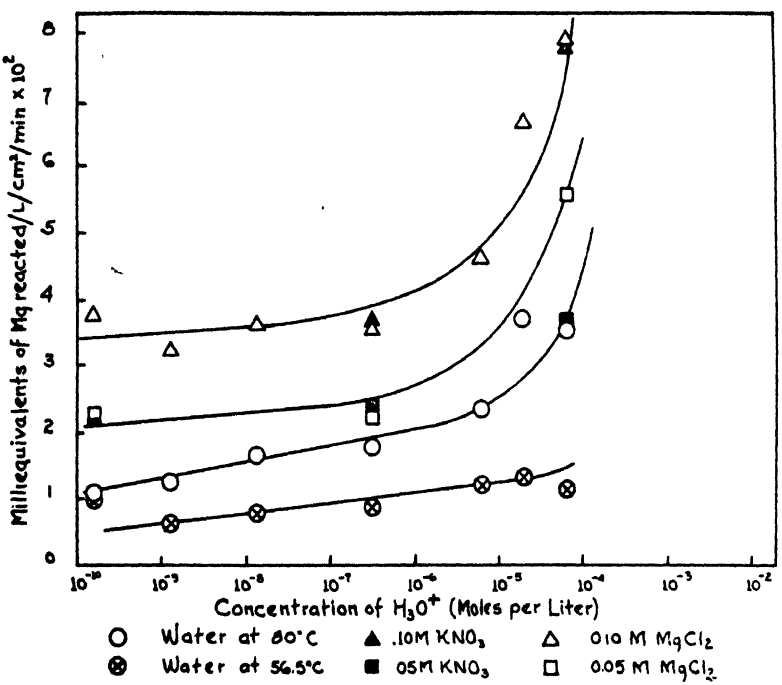

FIG. 9. WATER REACTION

electrolyte concentration, since this would not alter the general relationship appreciably.

In earlier experiments on the water reaction the gas evolution method was employed. In these experiments the evolution of gas did not start immediately and its subsequent evolution was not uniform. The metal became covered with an adherent film, and an insoluble compound was dispersed through the solution. In the presence of magnesium chloride or magnesium acetate, constant evolution of gas was obtained over a short interval. The results were similar to those in figure 9. See also reference 12.

TABLE 13

Acetic acid experiments at 25°C.

Acid base ratio = 1 to 1

EXPERIMENT NO.	R.P.M.	CM. PER MINUTE	*k* AT EXPERIMENT SPEED	*k* AT 2000	PER CENT REACTION	INITIAL ACID CONCENTRATION
84	0	0	0.0873		26.2	0.0485
45	0	0	0.0912		28.0	0.050
38	0	0	0.1047		45.0	0.050
39	0	0	0.1047		76.0	0.050
40	0	0	0.1047		15.1	0.050
41	0	0	0.1047		21.6	0 050
42	0	0	0.1047		31.8	0 050
85	425	1000	0.215	0.276	52.7	0.0485
46	425	1000	0.210	0.270	52.9	0.050
82	850	2000	0.281	0.281	62.6	0.0485
83	850	2000	0.274	0 274	61.6	0.0485
5	860	2180	0.289	0.282	19.8	0.0705
4	860	2190	0.295	0.285	20.7	0.0236
3	860	2210	0.310	0.297	21.7	0.0472
2	860	2230	0.302	0.290	21.4	0 0943
1	860	2250	0.290	0.277	10.0	0.382
25	800	2870	0.335	0.294	56.8	0.049
24	800	3790	0.357	0.284	62.5	0.098
81	1700	4010	0.403	0.313	75 7	0 0485
26	800	4660	0.395	0.292	73.4	0.0245
18	1200	5825	0.424	0.288	69.8	0.0980
74	2550	6040	0.426	0.287	77.9	0.051
75	2550	6040	0.437	0.294	78.5	0.0485
76	2550	6040	0.437	0.294	78.5	0.0485
20	1200	6240	0.430	0.286	73.1	0 0245
19	1200	6320	0.424	0.282	76.9	0.0490
15	2000	7240	0.438	0.277	79.4	0.0989
12	2000	7390	0.453	0.284	81.2	0.0989
6	2000	7430	0.468	0.292	82.2	0 0989
78	3400	8020	0.465	0.283	80.4	0.0485
79	3400	8020	0.473	0.287	81.0	0.0485
77	3400	8060	0.479	0.291	81.5	0.0485
23	2000	9550	0.496	0.284	74.5	0.0245
21	2000	9620	0.471	0.267	76.3	0.0989
9	2000	9740	0.490	0.277	90.5	0.0989
16	2000	9740	0.896	0.280	91.1	0.0495
14	2000	9780	0.503	0.284	91.2	0.0247
7	2000	9810	0.505	0.285	91.3	0.0495
11	2000	9810	0.487	0.276	90.5	0.0247
13	2000	9840	0.510	0.288	91.7	0.0495
17	2000	9840	0.496	0.280	91.4	0.0247
8	2000	9940	0.505	0.284	91.5	0.0247
22	2000	10350	0.504	0.287	78.4	0.0490
10	2000	11760	0.498	0.268	94.2	0.0490
				Av. = 0.284		

EXPERIMENTS WITH WEAK ACIDS

When a weak acid such as acetic acid is dissolved in water, there exists the usual double acid–base equilibrium.

$$\underset{\text{Acid 1}}{CH_3COOH} + \underset{\text{Base 2}}{H_2O} \rightleftarrows \underset{\text{Acid 2}}{H_3O^+} + \underset{\text{Base 1}}{CH_3COO^-} \qquad (11)$$

TABLE 14

Summary of acetic acid experiments at 25°C. and 2000 cm. per minute stirring speed

Acid base ratio = 1 to 1. Total ionic strength kept constant at 0.1 *M* with sodium chloride

NUMBER OF DUPLICATE EXPERIMENTS	INITIAL ACETIC ACID CONCENTRATION	CONCENTRATION OF ACETATE	MILLIEQUIVALENTS PER LITER PER CM² PER MINUTE
	M	*M*	
8	0.0246	0 0246	0 0066
1	0.0472	0 0472	0.0132
18	0 0495	0 0495	0.0132
2	0.0705	0.0705	0 0188
1	0.0943	0.0943	0.0258
8	0.0985	0.0985	0 0262
2	0.200	0.200	0.0478
1	0.382	0.382	0 1000

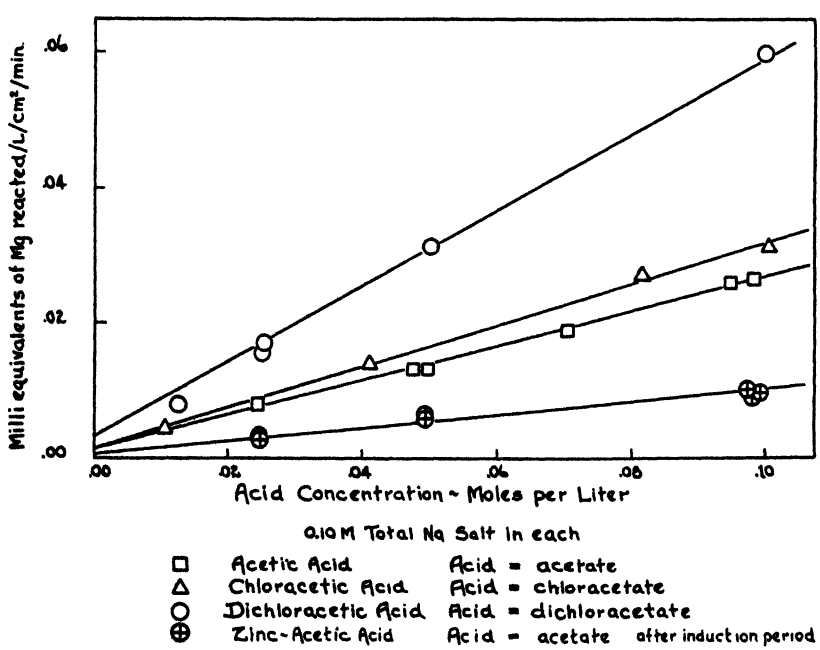

FIG. 10. REACTION WITH ACETIC ACID, CHLOROACETIC ACID, DICHLOROACETIC ACID

Since the reaction does not go completely to the right as in the case of a strong acid, there are, besides water, two acids, H_3O^+ and CH_3COOH. The problem, quite apart from the consideration of whether the reaction rate is controlled by diffusion or a chemical process, is whether the proton is brought to the metal by the H_3O^+ ion or the CH_3COOH molecule, or both. If it were brought by the H_3O^+ ion alone, then the rate would be given by equation 10 and the function of the acetic acid would be to supply more hydrogen ion. If both the H_3O^+ ion and the CH_3COOH molecule bring protons, the velocity should be represented by the equation

$$v = k_w + k_{H_3O^+}C_{H_3O^+} + k_{HAc}C_{HAc} \tag{12}$$

Of course, there might exist a medium effect of acetic acid which would alter $k_{H_3O^+}$ in equation 10.

To test equation 12 it is necessary to carry out a series of experiments at

TABLE 15

Summary of experiments with acetic acid at elevated temperature

NUMBER OF DUPLICATE EXPERIMENTS	TEMPERATURE	$\frac{1}{T} \times 10^4$	AVERAGE k_{2000}	LOG k_{2000}	HEAT OF ACTIVATION A	
	degrees C.					
2	0	36.6	0.0794	−1.100	k_{25}/k_0	8,250
35	25	33.5	0.284	−0.546		
13	27	33.35	0.366	−0.436	k_{27}/k_0	9,750
9	35	32.5	0.506	−0.296	k_{35}/k_{25}	10,700
5	56.5	30.0	0.611	−0.214	$k_{56.5}/k_{25}$	5,000
3	76	38.65	0.698	−0.156	k_{76}/k_{25}	4,000
5	80.2	28.3	1.100	+0.042	$k_{80.2}/k_{25}$	5,200

constant hydrogen-ion concentration and varying acetic acid concentration. Actually at 25°C. k_w is negligible, and at hydrogen-ion concentrations around $1 \times 10^{-5}M$ the term $k_{H_3O^+}C_{H_3O^+}$ becomes almost negligible, so that $v = k_{HA_c} C_{HA_c}$ if our hypothesis is correct. To minimize the change in Kc, the classical dissociation constant of the acid, the experiments were carried out at constant ionic strength. In order to put the experiments on a comparable basis, the effect of stirring was determined (see table 13 and figure 5).

Table 14 summarizes the results with acetate buffers, and figure 10 shows the proportionality between the increase in the reaction rate and the concentration of acetic acid. Table 14 and figure 10 prove the validity of equation 12. The intercept in figure 10 represents the amount reacting by way of the hydrogen ion and the water. The effect of viscosity has

already been given in table 8. Table 15 gives the results at higher temperatures.

In figure 7 the logarithm of k is plotted against $1/T$; the slope of the line corresponds to a heat of activation of 9500 calories, or a temperature

TABLE 16

Data for hydrochloric acid–acetic acid experiment 3

H_0 for 0.025 M acetic acid = 70.2 cc.

TIME	HYDROGEN H_t	HYDROGEN DUE TO 0 01 M HCl	HYDROGEN DUE TO $HC_2H_3O_2$ PRESENT	$H_0 - H_t$	LOG $\frac{H_0}{H_0 - H_t}$
minutes	*cc*	*cc*	*cc.*		
1	8.0	6 0	2 0	68.2	0 0100
2	18 7	10 8	7 9	62.3	0 0520
3	25 0	14.5	10.5	59 7	0 0700
4	31.3	17 5	13 8	56 4	0 0950
5	36 9	19.8	17 1	53.1	0 1218
6	41.0	21 6	19 4	50 8	0 1405
7	45.3	23 0	22 3	47.9	0.1660
8	49.0	24 1	24 9	45 3	0 1905
9	52 0	24 9	27.1	43 1	0 2120
10	55.6	25 7	29 9	40 3	0 2412

TABLE 17

Summary of mixed acid experiments at 25°C.

EXPERIMENT NO.	HYDROCHLORIC ACID CONCENTRATION	ACETIC ACID CONCENTRATION	k_{2600} FOR THE ACETIC ACID	MILLIEQUIVALENTS PER LITER PER CM² PER MINUTE DUE TO 0 01 M H_3O^+	MILLIEQUIVALENTS PER LITER PER CM² PER MINUTE DUE TO $HC_2H_3O_2$	MILLIEQUIVALENTS PER LITER PER CM² PER MINUTE TOTAL	PER CENT DECREASE OF $HC_2H_3O_2$ DUE TO H_3O^+	PER CENT INCREASE OF H_3O^+ DUE TO $HC_2H_3O_2$
	M	*M*						
1	0 01	0 005	0 276	0 01263	0.00131	0.01394	0 223	1 6
2	0 01	0.010	0.281	0 01263	0 00267	0 01530	0 219	1 0
3	0.01	0.025	0.274	0 01263	0 00651	0.01914	0 218	0 5
4	0 01	0.050	0.285	0.01263	0 01353	0.02616	0 216	0 2
5	0.01	0.075	0 280	0.01263	0 01998	0 03261	0.214	0.1

coefficient k_{35}/k_{25} of 1.69. It should be pointed out that a few experiments at 80°C. and 76°C. gave lower values.

EXPERIMENTS WITH MIXTURES OF HYDROCHLORIC AND ACETIC ACIDS

In order to test further the idea that the proton is brought to the metal by the molecular acid, a series of experiments were carried out in mixtures of hydrochloric and acetic acids. The addition of acetic acid increased the

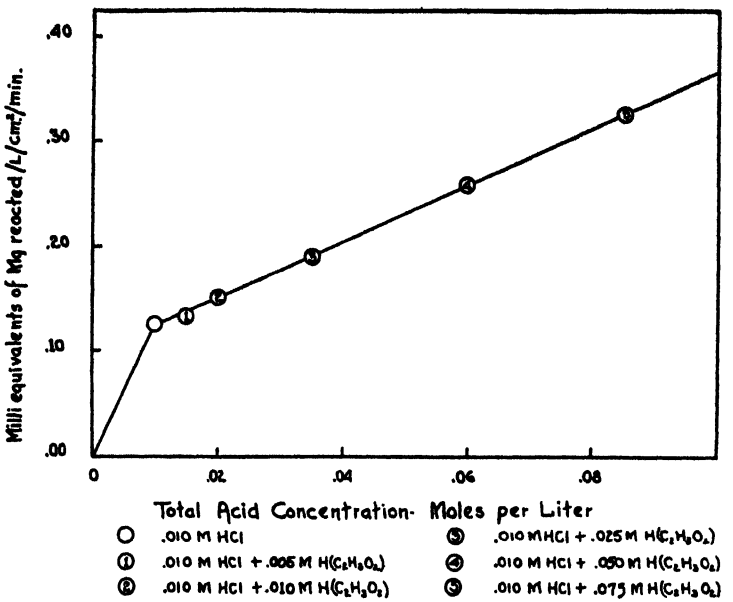

FIG. 11. REACTION WITH MIXED HYDROCHLORIC AND ACETIC ACIDS

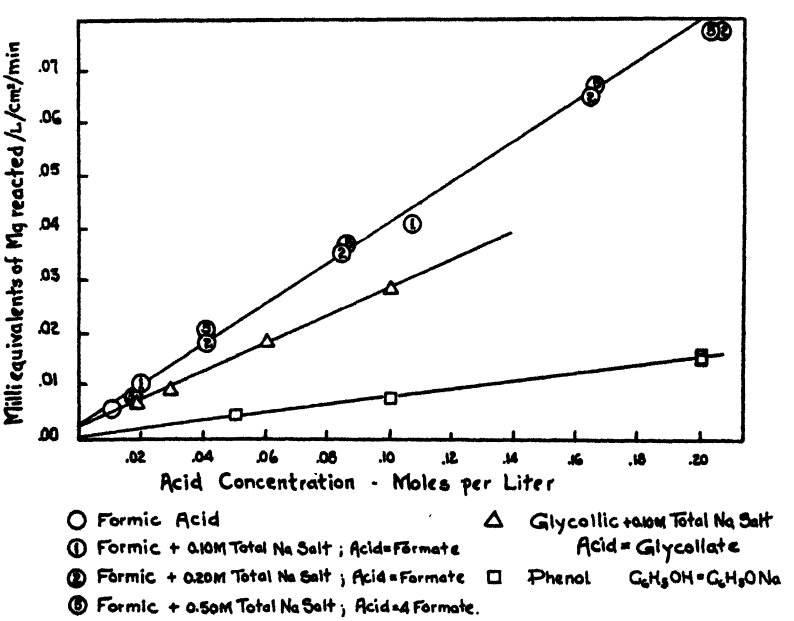

FIG. 12. REACTION WITH FORMIC ACID, GLYCOLLIC ACID, PHENOL

hydrogen-ion concentration slightly. If equation 12 holds, there should be a noticeable increase in rate upon the addition of acetic acid; if the hydro-

TABLE 18

Experiments with chloroacetic and dichloroacetic acids

Acid base ratio 1 to 1. 0.1 *M* total ionic strength

ACID CONCENTRATION	k_{2000}	MILLIEQUIVALENTS PER LITER PER CM.² PER MINUTE	PER CENT REACTION FOLLOWED
(a) Experiments with chloroacetic acid at 25°C.			
M			
0.0106	0.384	0.0037	44.2
0.0412	0.363	0.0142	23.8
0.0815	0.352	0 0271	63.5
0.1016	0.320	0.0309	21 5
(b) Experiments with dichloroacetic acid at 25°C.			
0.0125	0.662	0.00786	45.6
0.0250	0.645	0.0153	80.8
0.0252	0.675	0.0170	63.4
0 050	0.658	0.0312	91.8
0.100	0.622	0.0591	91.8

TABLE 19

Experiments with formic acid at 25°C.

ACID CONCENTRATION	ACID BASE RATIO	IONIC STRENGTH	k_{2000}	MILLIEQUIVALENTS PER LITER PER CM.² PER MINUTE	PER CENT REACTION FOLLOWED
M		*M*			
0.0103	Acid alone	—	0.438	0.00426	27
0.0205	1 to 1	0.2	0.436	0.00842	42
0.0214	1 to 1	0.1	0 400	0.00813	28
0.041	1 to 1	0.2	0 465	0.0181	54
0.041	4 to 1	0.05	0.512	0.0199	34
0 082	1 to 1	0.2	0.455	0.0352	48
0.082	4 to 1	0.05	0.492	0.0380	44
0.107	1 to 1	0.1	0.398	0.0402	23
0.164	1 to 1	0.2	0.430	0.0659	63
0.164	4 to 1	0.05	0.482	0.0750	40
0.205	1 to 1	0.2	0.410	0.0795	58
0.205	4 to 1	0.05	0.402	0.0785	15
2.068	Acid alone	—	0.430	0.8400	9

gen ion is the sole carrier, there should be very little change in rate. The method of calculation is indicated in table 16. Column 2 gives the total gas evolved, column 3 the gas evolved in 0.01 *M* hydrochloric acid solutions,

and column 4 the difference. A plot similar to figure 3 shows that the part of the reaction due to the acetic acid follows a first order law. Table 17 summarizes these results and shows the change in the hydrogen-ion concentration in each experiment. The average value of k_{HA_0} for the experiments is 0.280, as compared with 0.284 from the results in solution buffered with respect to the hydrogen ion. This is good evidence that whether the rate is controlled by a chemical process or one of diffusion the metal reacts with the molecular acid. This result is represented graphically in figure 11. The milliequivalents of magnesium reacted are plotted against the total acid concentration.

TABLE 20

Experiments with glycollic acid at 25°C.

Acid base ratio = 1

ACID CONCENTRATION	k_{2000}	MILLIEQUIVALENTS PER PER LITER PER CM.^{2} PER MINUTE	PER CENT REACTION FOLLOWED
M			
0.0175	0.357	0.00592	41
0.0298	0.306	0.00863	43
0.0595	0.354	0.0195	44
0.0993	0.303	0.0284	46

TABLE 21

Experiments with phenol

1 C_6H_5OH to 1 C_6H_5ONa

NUMBER OF DUPLICATE EXPERIMENTS	PHENOL CONCENTRATION	k_{2000}	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE
	M		
2	0.200	0.0778	0 01488
2	0.100	0.0815	0.00775
2	0 050	0.0764	0.00415

The slope of the first part of the line represents $k_{H_3O^+}$ and corresponds to the slope in figure 6. The slope of the second part of the line corresponds to that of the line for acetic acid in figure 10. It should be emphasized that the hydrogen-ion concentration has been increased less than two per cent by the addition of acetic acid, yet the rate is increased twofold.

Table 18 summarizes the experiments with monochloroacetic and dichloroacetic acids.

Figure 10 shows good proportionality between the increase in reaction rate and the acid concentration. The order is that of the acid strength. The intercept for dichloroacetic acid is lower than would be expected.

Table 19 and figure 12 give the results for formic acid. All experiments are calculated to a surface speed of 2000 cm. per minute using equation 9, using the same values for a and n as for acetic acid.

The results for glycollic acid are also represented in figure 12, the data being given in table 20. Again there is good proportionality between the increase in rate and the concentration of the molecular acid.

TABLE 22

Experiments with pyridinium ion

CONCENTRATION OF PYRIDINIUM	k_{2000}	MILLIEQUIVALENTS PER LITER PER CM.² PER MINUTE
M		
0.05	0.586	0.0278
0.05	0.581	0.0275
0.0375	0.559	0.01988
0.025	0 522	0.01238
0 025	0.516	0.01222
0.0125	0.432	0 00512
0 0125	0.438	0 0052
0 01	0 424	0.00402

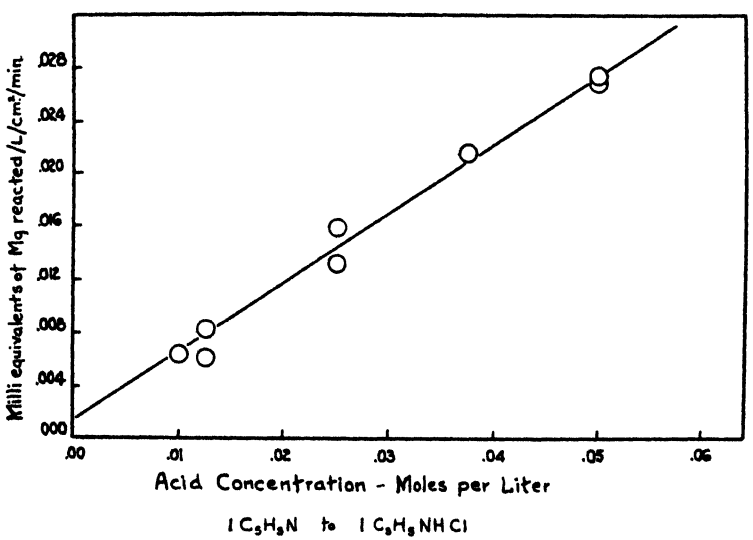

FIG. 13. REACTION WITH PYRIDINIUM ION

In order to show that in general molecular acids react with magnesium, a few experiments were carried out in phenol–phenylate buffers. Table 21 and figure 12 summarize the results.

Table 22 and figure 13 give the results with pyridinium–pyridine buffers.

In both cases equation 12 applies and the velocity constants are in accord with the lower strength of the acids.

TABLE 23

Experiments with citric and tartaric acids

NUMBER OF DUPLICATE EXPERIMENTS	ACID CONCENTRATION	k_{3000}	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE	PER CENT AVERAGE OF REACTION FOLLOWED
(a) Experiments with citric acid				
	M			
2	0.0473	1.13	0.0508	52.4
2	0.0310	1.08	0.0318	72.5
1	0.0236	1.07	0.0240	31.4
1	0.0118	1.16	0.0130	66.5
2	0.0104	1.14	0.0113	41.4
2	0.0081	1.13	0.0087	60.6
2	0.0039	1.10	0.0041	62.9
(b) Experiments with dihydrogen citrate ion				
2	0.05	0.494	0.0235	74.0
1	0.025	0.498	0.0119	57.8
1	0.0125	0.492	0.0058	82.0
2	0.0059	0.500	0.0028	30.0
(c) Experiments with monohydrogen citrate ion				
2	0.05	0.182	0 00866	82 0
1	0.025	0.185	0.00440	34.0
2	0.0125	0.187	0.00222	45.0
(d) Experiments with tartaric acid				
2	0.0243	0.730	0.0169	93.6
2	0.0180	0.710	0.0121	96.9
2	0.01205	0.702	0.0080	94.6
2	0.00578	0.710	0.0039	95.6
(e) Experiments with bitartrate ion				
2	0.0502	0.220	0.0105	82.3
2	0.0442	0.216	0.0091	84.5
2	0.0380	0.230	0.0083	84.5
1	0.0250	0.225	0.0054	87.5
2	0.0067	0.218	0.0014	84.5

In the case of dibasic and tribasic acids such as tartaric and citric acids, it was necessary to determine the velocity constants for the several acids present. In order to do this it was necessary to obtain the classical disso-

ciation constants at suitable ionic strengths and to calculate the concentrations of the various acids present. The necessary values for tartaric and citric acid were obtained from the literature (2, and especially 21). The method of calculating the velocity constants was similar to that used for the mixtures of acetic and hydrochloric acids. The results are summarized in table 23, and the proportionality of the increase in rate due to each acid is shown in figure 14.

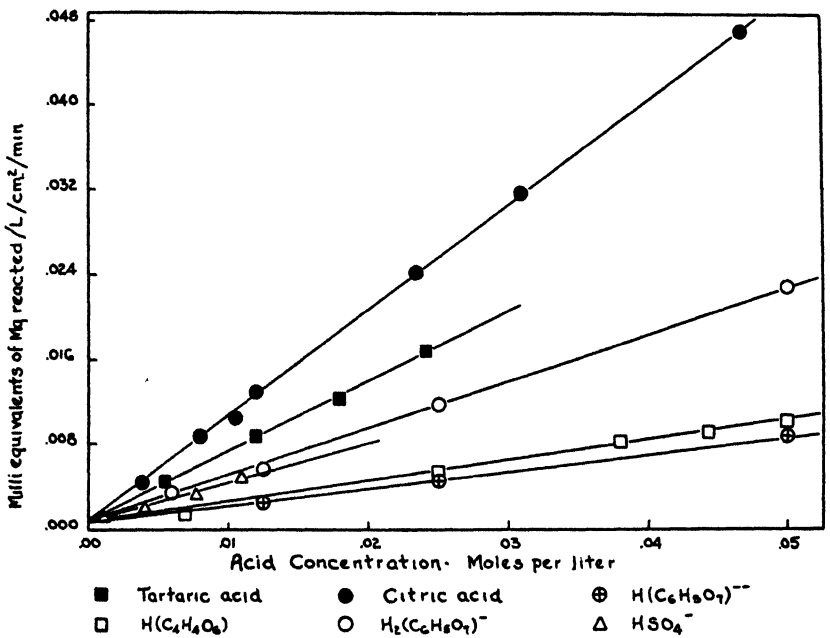

FIG. 14. REACTION WITH TARTARIC ACID, CITRIC ACID, $H(C_4H_4O_6)^-$, $H_2(C_6H_5O_7)^-$, $H(C_6H_5O_7)^{--}$, AND HSO_4^-

EXPERIMENTS WITH ZINC

Experiments on the dissolution of zinc in hydrochloric acid and in acetic acid were carried out under the same experimental conditions as those prevailing in the experiments with magnesium. With zinc an induction period of twenty to twenty-five minutes was noticed, after which the evolution of hydrogen followed the same law as in the case of magnesium. Beginning at the end of the induction period, k_{2000} and the milliequivalents reacted were calculated in the same way as in the experiments with magnesium.

Table 24 gives the data for hydrochloric acid and figure 6 shows the proportionality between the rate and the hydrogen-ion concentration, after the induction period.

TABLE 24

Experiments with zinc and hydrochloric acid at 25°C.

Weight determinations

ACID CONCENTRATION	CONCENTRATION OF ADDED SALT	k_{2000}	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE
M	*M*		
0.1063	0.10 NaCl	0.375	0.03775
0.0530	0.10 NaCl	0.359	0.01805
0.0530	0.10 NaCl	0.361	0.01815
0.0265	0.10 NaCl	0.375	0.00944
0.0265	0.10 NaCl	0.365	0.00919
0.0133	0.10 NaCl	0.359	0.00454
0.050	0.10 NaCl	0.375	0.00178
0.050	0.10 KNO_3	5.18	0.0245
0.050	0.10 KNO_3	5.23	0.0248
0.100	0.10 KNO_3	6.63	0.0628

TABLE 25

Experiments with zinc and buffered acetic acid solutions at 25°C.

Weight determinations

ACID CONCENTRATION	CONCENTRATION OF ADDED SALT	CONCENTRATION OF SODIUM ACETATE	k_{2000}	MILLIEQUIVALENTS PER LITER PER CM.^{2} PER MINUTE
M	*M*	*M*		
0.0980		0.100	0.107	0.00997
0.0980		0.100	0.097	0.00902
0.0490	0.050 NaCl	0.050	0.124	0.00577
0.0490	0.050 NaCl	0.050	0.130	0.00605
0.0245	0.025 NaCl	0.025	0.114	0.00265
0.0245	0.025 NaCl	0.025	0.118	0.00275
0.100	0.100 NaCl		0.105	0.00991
0.100	0.100 KNO_3		4.10	0.389
0.100	0.100 KNO_3		4.20	0.399

TABLE 26

Comparison of reaction rates of magnesium and zinc at 25°C.

METAL	k_{2000} FOR HCl	k_{2000} FOR HCl + 0.05 *M* KNO_3	k_{2000} FOR $HC_2H_3O_2$	k_{2000} FOR $HC_2H_3O_2$ + 0.1 *M* KNO_3
Mg	1.33	1.20	0.284	0.280
Zn	0.367	5.20	0.113	4.10

Table 25 and figure 10 present the results obtained in acetate–acetic acid buffer solutions and show the proportionality between the rate and the concentration of molecular acid, after the induction period. In both cases the addition of potassium nitrate has a marked effect on the rate. It was

found, as King and Braverman found (17), that potassium nitrate has very little, if any, effect on the rate of solution of magnesium. The results obtained with the two metals are given in table 26.

There is evidence that at high concentrations of potassium nitrate, zinc undergoes other reactions. In regard to the absence of the effect of potassium nitrate upon the dissolution of magnesium, attention is called to the recent results of Whitby (26), who found that when magnesium reacts with acids, in the presence of air, no oxygen is consumed.

DISCUSSION OF THE RESULTS

In table 2 the relation between the velocity and the surface was clearly shown. Whether the measured surface represents the actual surface reacting or is proportional to it cannot be determined by these experiments. It may be that active areas of the surface are being used and that the chemical process involves adsorption and activation (25) at the surface, but reproducibility of the results would indicate that this is not the case.

In the water reaction sodium chloride and magnesium salts caused an increase in the rate of reaction. One explanation of the effect is that the salt dissolves the magnesium oxide or forms a soluble complex salt (19). This prevents the formation of insoluble coatings which might impede the reaction. Another explanation favored by Bancroft (1) is that the added salts peptize the magnesium oxide coating.

As has been indicated throughout the paper, the most difficult problem connected with a reaction at a metal–liquid interface is to decide whether the rate-controlling process is the chemical reaction or diffusion. King and Braverman (17), after a study of the reaction of zinc with acids following along the lines of the preliminary publication by Kilpatrick and Rushton (16), concluded, "It is impossible to decide at present whether other acids than H_3O^+ react directly with magnesium, zinc, cadmium, and marble, since previous experiments have measured rates controlled largely by diffusion rates." They reached this conclusion on the basis of certain observed facts which, in general, have been accepted as criteria of the validity of the diffusion rate theory. These are:

(1) Different solids dissolve at nearly the same rate.
(2) Stirring has a marked effect on the rate.
(3) The rate of solution is inversely proportional to the viscosity.
(4) The rates observed follow diffusion coefficients for comparable experimental conditions.
(5) The temperature coefficients are small compared to those of chemical reactions.

Consider the first point outlined above. Table 27 gives the only comparable results on a milliequivalent basis. These results are to be compared with table 26 in the experimental part of this paper. The results do not bear out a diffusion controlled process.

In regard to the second point, the effect of stirring has been thoroughly studied and the relationship $k = aR^n$ is difficult to explain on the basis of any chemical rate theory. However, owing to temperature effects it is not practicable to extend the study to such surface speeds that the thickness of the so-called diffusion layer would be such that the rate of the chemical reaction would be measured.

The results of experiments to test the effect of change in viscosity are definitely contradictory to the diffusion theory in the case of salts, and for non-electrolytes the inverse proportionality is at best qualitative.

If one attempts to compare the velocity constants for the different acids with the meager data on diffusion coefficients existing in the literature, one finds that the order for decreasing velocity constants is as follows: the acid H_3O^+, formic acid, acetic acid, citric acid, tartaric acid, and phenol. On the other hand, the diffusion coefficients are in the following order: hydrochloric acid, formic acid, acetic acid, phenol, tartaric acid, and citric acid. Of course, the exponents of the idea that the H_3O^+ ion is the only

TABLE 27

Results of King and Braverman at 25°C.

Surface speed = 24,000 cm. per minute

METAL	MILLIEQUIVALENTS PER LITER PER CM.² PER MINUTE FOR 0.007 *M* HCl + 0.05 *M* KNO_3	MILLIEQUIVALENTS PER LITER PER CM.² PER MINUTE FOR 0.03 *M* $HC_2H_3O_2$ + 0.05 *M* KNO_3
Mg	0.0235	0.031
Zn	0.0215	0.032

acid present might not consider that it was necessary for acids other than the H_3O^+ to diffuse to the metal. It has been shown that this conclusion is not in accord with the experimental results. It may be stated that the indefiniteness of the diffusion theory makes it especially difficult to distinguish between diffusion and any other rate-controlling process. This vagueness is particularly evident when one considers the reaction of magnesium with acids at temperatures above 50°C. It has been experimentally demonstrated that there are at least two reactions in aqueous solutions of strong acids. First, a water reaction independent of the hydrogen-ion concentration, and second, a reaction dependent on the hydrogen-ion concentration. If one assumes that the diffusion process consists of a diffusion of a hydrogen ion through a layer poorer in hydrogen ions up to the metal surface, and that this is the rate-controlling process, with subsequent diffusion of magnesium ion away from the metal surface, then what is the diffusion layer involved in the reaction of magnesium with water, which is independent of the hydrogen-ion concentration? It may be pointed out that this layer cannot be a film of hydrogen because the rate is unchanged by the addition of a depolarizer.

The temperature coefficient for the reaction with the hydrogen ion is 1.7 for a 10-degree interval. Centnerszwer (8) reports 1.2 for unstirred and stirred solutions. Bonsdorff (4) obtains a value which decreases markedly with increasing temperature. The temperature coefficient for the water reaction is 1.34. Still it is difficult to picture a diffusion mechanism for the water reaction. A general criterion of the statement that chemical reactions usually have temperature coefficients greater than 2 for a 10-degree interval is that these temperature coefficients usually apply to reactions taking place in one phase and not to reactions at an interface.

In those cases where an induction period exists, i.e., where the initial rate is slower than that in a later part of the reaction, the rate during the induction period is probably governed by chemical reactions. This must be the case even though conditions favor a diffusion controlled reaction, irrespective of the induction period. If chemical reactions have high temperature coefficients, the temperature coefficient for the induction period should be greater than that of the subsequent reaction, if the latter is controlled by diffusion. There are no data in the literature sufficiently consistent to test this point.

The arguments in favor of a chemical process controlling the rate are:

(1) High temperature coefficient.

(2) Proportionality of rate to the concentration of acid present or, in general, for a number of acids

$$v = k_1C_{A_1} + k_2C_{A_2} + k_3C_{A_3} + \ldots.$$

(3) Independence of the rate of the H_3O^+ ion concentration in the case of weak acids.

(4) A linear relationship between the logarithm of the velocity constant and the logarithm of the acid strength.

The temperature coefficient has been discussed. It has been shown experimentally that at constant H_3O^+ concentration the rate of reaction is proportional to the concentration of the other acids present. This has been clearly demonstrated throughout the experimental work. With the phenol–phenylate buffers the H_3O^+ concentration was of the order of 1×10^{-10} M, and at 25°C. neither the reaction with the H_3O^+ ion nor the water reaction is more than detectable. From the experiments at 80°C. one calculates that at 25°C. by the water reaction 0.0001 milliequivalent of magnesium reacts per cm.^{2} per minute per liter. Yet in the presence of 0.1 M phenol 0.00775 milliequivalent reacts. It should also be remembered that the rate is proportional to the concentration of phenol.

That the rate of reaction, in the case of weak acids, is independent of the hydrogen-ion concentration is shown by the data in the tables referring to the acids in question. The rate is practically independent of the acid–base

ratio in the buffer solutions. For the water reaction the point is illustrated by table 12 and figure 8.

Arguments two and three, which were given in favor of a chemical process controlling the rate, might also be advanced in favor of a modified diffusion explanation if one considers the problem from the standpoint of the extended theory of acids. In other words, if it is postulated that diffusion governs the rate, it must be admitted that in the case of an acid like acetic acid the diffusion of the molecular acid to the metal must be considered, as well as the diffusion of the hydrogen ion. Subsequently, two reactions take place at the surface of the metal. The reactions formulated by equation 1

$$H_3O^+ + e \rightarrow H + H_2O$$
$$HAc + e \rightarrow H + Ac^-$$

would apply in principle to any acid. However, it is difficult to picture a diffusion mechanism for the water reaction. Whatever the rate-controlling process in these reactions, the principle that they must be considered from the viewpoint of the extended theory of acids is the thesis of this work.

Although King and Braverman conclude that it has not been proven that acids other than the H_3O^+ react with metals, they are forced to fall back on the extended theory of acids to explain their results. This is particularly true in their experiments with sodium acetate and acetic acid, and with citric and tartaric acids. In this connection the experiments in mixtures of hydrochloric and acetic acids recorded in table 16 should be noted. It is again emphasized that there are two reactions present, that due to H_3O^+ and that due to molecular acetic acid. k (acetic acid) calculated from these experiments is in agreement with k (acetic acid) calculated from experiments at low hydrogen-ion concentrations. In other words, the hydrogen-ion concentration has been changed from 1×10^{-5} M to 1×10^{-2} M and yet k (acetic acid) is unchanged.

In the preliminary paper the velocity constant was related to the acid strength of the reacting acid by an equation of the type

$$k_a = G_1 K_A^{\alpha} \tag{13}$$

where k_a is the velocity constant and K_A the dissociation constant of the reacting acid. This equation cannot be expected to hold exactly even in homogeneous catalysis for different types of acid. By different types is meant different charge types such as H_3O^+, HSO_4^- and uncharged acids like acetic acid and water. In fact the relationship seems to hold exactly only for an homologous series (15). The effect of the charge of the base in a reaction showing basic catalysis has been demonstrated by Brönsted and Volquartz (7), and more recently by Pedersen (22).

Furthermore, in addition to the difference in type, the statistical factor

must be taken into account. When this is done, the general equation becomes

$$k_a = G_1 K_A{}^x q^x p^{1-x} \tag{14}$$

where k_a is the velocity constant for the acid considered, G_1 is a constant, K_A is the acid strength constant, q the number of positions at which a proton can be attached to the molecule of the conjugate base, p the number of ionizable hydrogen atoms in the molecule, and x has a value greater than

TABLE 28

Data necessary for testing relationship between velocity constant and acid strength

ACID	q	p	K_A	LOG $\frac{q}{p} K_A$	k_{2000}	LOG $\frac{k}{p}$
H_3O^+	1	1	55 6	1 745	1.33	0 124
Bisulfate	4	1	5 1 $\times 10^{-2}$	−0 690	0 519	−0 285
Dichloroacetic	2	1	5 $\times 10^{-2}$	−1 000	0.592	−0 228
Tartaric	2	2	1.45 $\times 10^{-3}$	−2 838	0.712	−0 448
Chloroacetic	2	1	1 41 $\times 10^{-3}$	−2.550	0 355	−0.450
Citric	2	3	1 3 $\times 10^{-3}$	−3.160	1.119	−0 428
Formic	2	1	1 8 $\times 10^{-4}$	−3 444	0 443	−0.354
Glycollic	2	1	1 36 $\times 10^{-4}$	−3 566	0 327	−0 485
Dihydrogen citrate	4	2	4 7 $\times 10^{-5}$	−4 027	0 496	−0.605
Acetic	2	1	1 8 $\times 10^{-5}$	−4 444	0 284	−0 547
Bitartrate	4	1	1 27 $\times 10^{-5}$	−4.294	0.223	−0 652
Pyridinium	1	1	7 4 $\times 10^{-6}$	−5 131	0 507	−0 295
Monohydrogen citrate	6	1	2.2 $\times 10^{-6}$	−4 879	0.185	−0 733
Phenol	1	1	1 1 $\times 10^{-10}$	−9 959	0 0809	−1 092
Water	1	1	1 1 $\times 10^{-16}$	−15 959	2 28 $\times 10^{-4}$	−3.432
Results of Tarle						
H_3O^+	1	1	55 6	1 745	1.33	0 090
1,2,5-Dioxybenzoic	2	1	1 8 $\times 10^{-3}$	−2.666	0.774	−0 111
β-Resorcylic	2	1	5.15 $\times 10^{-4}$	−2 987	0 511	−0 292
Tricarballylic	2	3	2 2 $\times 10^{-4}$	−3.839	0.489	−0 788
Acetic	2	1	1.8 $\times 10^{-5}$	−4 444	0.390	−0 409

zero and less than one. To test this relationship the equation can be put in the form

$$\frac{k_a}{p} = G_1 \left(K_A \frac{q}{p} \right)^x$$

If log $\frac{k_a}{p}$ is plotted against log $\frac{q}{p} K_A$, the points for each charge type should fall in a straight line with slope x and intercept G_1. Table 28 summarizes

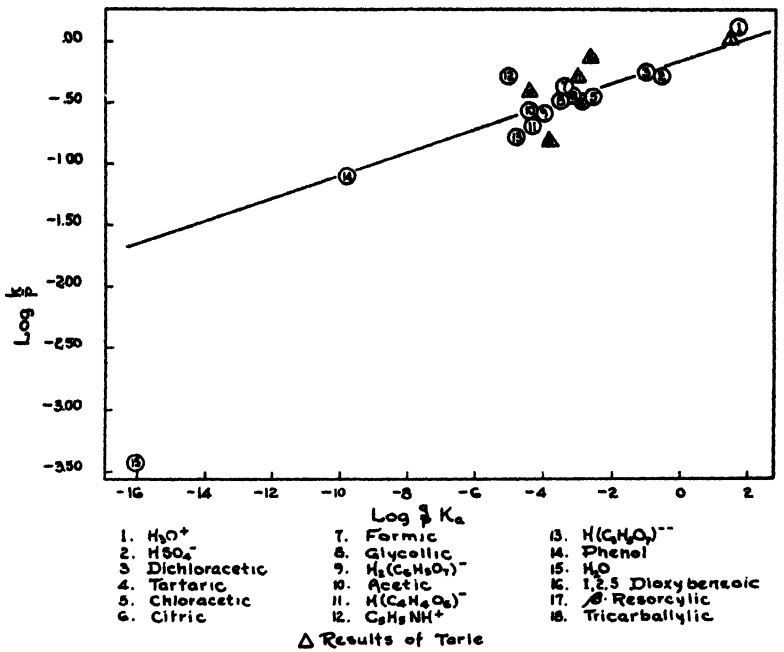

FIG. 15. RELATION BETWEEN VELOCITY CONSTANT k AND ACID STRENGTH

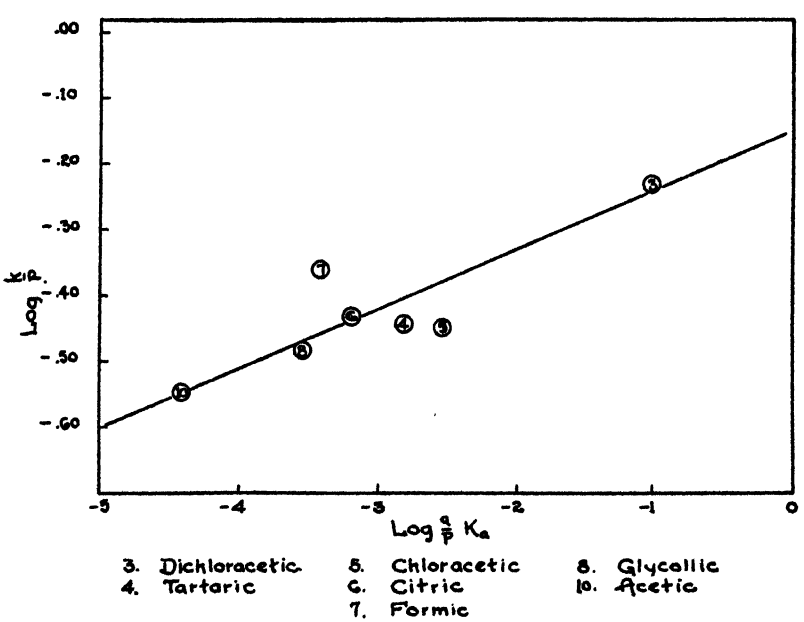

FIG. 16. RELATION BETWEEN VELOCITY CONSTANT k AND ACID STRENGTH

the data necessary for testing the general relationship between the velocity constant and the acid strength of the different acids.

Figure 15 shows the relationship for all acids studied and in addition includes the results of Tarle (24). Tarle's results are not strictly comparable with those in this work, since his data are not complete enough to determine surface speed.

Figure 16 shows on a larger scale the small section of figure 15 which covers the carboxylic acids. While the agreement with the theory is not exceptional, it is to be noted that there is a general relationship between the velocity constant and the acid strength. From theoretical considerations it is to be expected that for equal strength the positively charged acids will show greater velocity constants. This is borne out by the position of hydrogen ion and pyridinium ion in the plot. From the same considerations it is to be expected that a negatively charged acid will fall below the line drawn through the uncharged acids. This is also evident from the plot. The value of x is 0.091.

SUMMARY

(1) Rates of solution of magnesium in aqueous solution of acids have been determined by four different experimental methods, and the results are found to be reproducible and in agreement for the different samples of magnesium.

(2) The kinetic law for the reaction has been derived and extensively tested over the whole course of the reaction. The general kinetic equation is

$$v = k_1C_{H_2O} + k_2C_{H_3O^+} + k_3C_A + \ldots\ldots \text{ etc.}$$

where A represents an acid other than the H_3O^+ or water.

(3) For strong acids the primary reaction is with the H_3O^+ ion.

(4) For weak acids the rate of reaction is not proportional to the hydrogen-ion concentration, but rather the increase in rate is proportional to the concentration of the acid present.

(5) A relation has been found between the surface speed of the metal and the rate of its reaction.

(6) The effect of viscosity has been investigated.

(7) The temperature coefficient has been determined for the water reaction, the H_3O^+ reaction, and the molecular acetic acid reaction.

(8) The results have been discussed from the standpoint of the diffusion theory and the Brönsted-Kilpatrick theory. The results are definitely not in agreement with the "old diffusion theory," but may be thought of in terms of a modified diffusion theory based on the extended theory of acids. However, any modification must account for the water reaction.

(9) On the basis of the Brönsted-Kilpatrick theory the velocity constants have been related to the acid strength.

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THE CALCULATION OF PARTIAL MOLAL SOLUTE QUANTITIES AS FUNCTIONS OF THE VOLUME CONCENTRATION, WITH SPECIAL REFERENCE TO THE APPARENT MOLAL VOLUME[1]

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The partial molal solute quantity $\overline{G}_2$ is important and frequently used in thermodynamic calculations. Many methods have been developed for calculating $\overline{G}_2$ from a particular extensive property, usually through the intermediate apparent molal quantity Φ (G_2), but most of these are based upon the weight concentration. Lewis and Randall (7) outlined various methods, both analytical and graphical. To mention only a few of the other methods most recently used: La Mer and Gronwall (6) analytically derived a fourth order equation for the partial molal volume as a function of the molality. Adams and Gibson (1) calculated the partial specific volume from the apparent specific volume plotted against the square root of the weight fraction. Randall and Rossini (9) developed an equation for calculating the partial from the apparent molal heat capacity as a function of the square root of the molality. Young and Vogel (14) discussed at length methods of calculating partial molal quantities in general, but dealt only with equations based on weight concentration.

Within recent years, however, experimental evidence has shown, in the case of most electrolytes, a linear relationship between many apparent molal properties and the square root of the volume concentration, which holds even in concentrated solutions. This relationship in the case of $\Phi(V_2)$, discovered by Masson (8), has been checked by the very careful measurements of Geffcken (2, 3) and also by Scott (13). Moreover, Redlich and Rosenfeld (10) derived from the Debye-Hückel theory an equation showing that $\overline{V}_2$, and hence also $\Phi(V_2)$, should be linear functions of $c^{\frac{1}{2}}$ at very *low* concentrations. The same relationship was found in the case of the apparent molal compressibility by the present author, who discussed the experimental and theoretical aspects of this problem in a recent article (4). Such a simple and general relationship seems an ideal starting

[1] Some conclusions in this article were briefly discussed in the Symposium on Electrolytes held at the Washington meeting of the American Chemical Society, March, 1933.

point in calculating partial molal quantities. This paper indicates how such calculations may be made.

DEFINITIONS

G is any extensive property of a solution containing n_1 and n_2 moles of solvent and solute of molecular weights M_1 and M_2, respectively. The corresponding *apparent* molal solute property is defined thus:

$$\Phi(G_2) = (G - n_1\overline{G}_1^0)/n_2 \tag{1}$$

and the *partial* molal properties of solute and solvent are given by the equations

$$\overline{G}_2 = \left(\frac{\partial G}{\partial n_2}\right)_{n_1} \tag{2}$$

and

$$\overline{G}_1 = \left(\frac{\partial G}{\partial n_1}\right)_{n_2} \tag{2'}$$

The superscript ^{0} is used at zero concentration. d and d_1 are the densities of solution and of solvent, c is the concentration (moles of solute per liter of solution), and m is the molality (moles of solute per 1000 g. of water).

The apparent molal volume is defined by any of the following equations:

$$\Phi(V_2) = \frac{V - n_1\overline{V}_1^0}{n_2} \tag{3}$$

$$\Phi(V_2) = \frac{1000}{c} - \frac{1}{d_1}\left[\frac{1000d}{c} - M_2\right] \tag{4}$$

$$\Phi(V_2) = \frac{1000}{c} - \frac{1000}{md_1} \tag{5}$$

CALCULATION OF THE APPARENT MOLAL VOLUME

The usual method is to calculate $\Phi(V_2)$ directly from density measurements, using equation 4. These values are then plotted against $c^{\frac{1}{2}}$ and the best curve fitted to them. The following method is, however, much simpler. Rearrange equation 4 as follows:

$$1000\left(\frac{d_1 - d}{c}\right) = d_1\Phi(V_2) - M_2 \tag{6}$$

If we now plot $F \equiv 1000\left(\frac{d_1 - d}{c}\right)$ against $c^{\frac{1}{2}}$ we can calculate Φ as a function of $c^{\frac{1}{2}}$, for the intercept

$$F^0 = d_1\Phi^0 - M_2$$

and the slope

$$\frac{\partial F}{\partial c^{\frac{1}{2}}} = d_1 \frac{\partial \Phi}{\partial c^{\frac{1}{2}}}$$

hence

$$\Phi^0 = \frac{F^0 + M_2}{d_1} \tag{7}$$

and

$$\frac{\partial \Phi}{\partial c^{\frac{1}{2}}} = \frac{1}{d_1} \frac{\partial F}{\partial c^{\frac{1}{2}}} \tag{8}$$

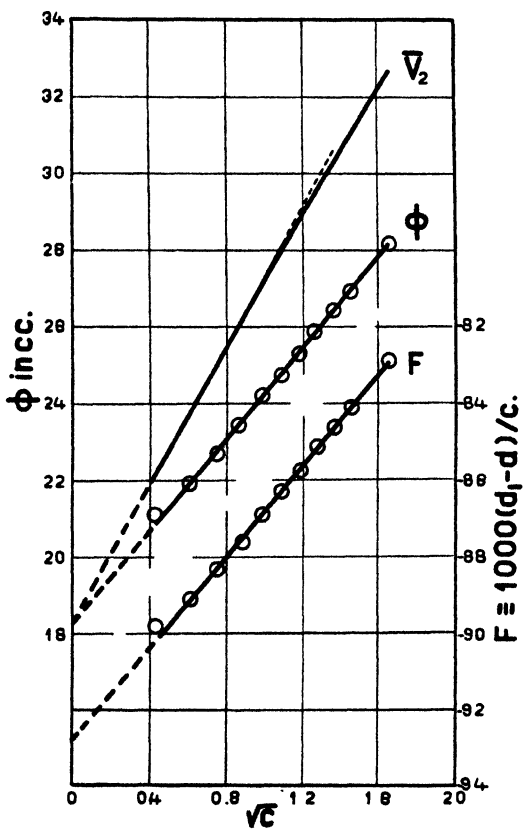

FIG. 1. Φ AND F FOR CALCIUM CHLORIDE AT 25°C.

The experimental points are thus smoothed by the F plot, and the extra calculations, involving the d_1 and M_2 terms, are required only *once*, to obtain the final values of the coefficients.

In order to illustrate the method, the density data for calcium chloride

at 25°C., taken from the International Critical Tables (5), have been used to calculate F and Φ. Both are linear functions[2] of $c^{\frac{1}{2}}$ up to 3 c as may be seen in figure 1. The equation for F was found to be

$$F = -92.81 + 5.97c^{\frac{1}{2}}$$

whence,

$$\Phi = 18.24 + 5.99c^{\frac{1}{2}}$$

A direct plot of Φ values gives the almost identical result,

$$\Phi = 18.26 + 5.99c^{\frac{1}{2}}$$

The method of calculating Φ from F is not limited to the special case in which each is a linear function of $c^{\frac{1}{2}}$. If F is *any* known function of $c^{\frac{1}{2}}$, the corresponding equation for Φ can easily be calculated. Thus, if

$$F = F^0 + F\ (c^{\frac{1}{2}})$$

$$\Phi = \frac{F^0 + M_2}{d_1} + \frac{1}{d_1}\ F\ (c^{\frac{1}{2}}) \tag{9}$$

W. C. Root (12) has derived a useful equation for the density of a solution obeying Masson's law. Using molal concentration this becomes

$$d = d_1 + Ac + Bc^{\frac{3}{2}}$$

This equation may be generalized as follows:

$$d = d_1 - \frac{F^0 c}{1000} - \frac{c}{1000}\ F\ (c^{\frac{1}{2}}) \tag{10}$$

or,

$$d = d_1 + \left[\frac{M_2 - d_1\Phi^0}{1000}\right] c - \frac{d_1 c}{1000}\ \Phi\ (c^{\frac{1}{2}}) \tag{11}$$

In particular, if Φ can be expressed as a power series in terms of $c^{\frac{1}{2}}$, the corresponding equation for the density will be

$$d = d_1 + Ac + Bc^{\frac{3}{2}} + Cc^2 + - - \tag{11'}$$

where the coefficients A, B, C are calculable from those of the Φ equation.

THE CALCULATION OF $\overline{G}_2$ FROM $\Phi(G_2)$

The equation connecting these two functions is derived as follows: Differentiating equation 1 gives

$$\overline{G}_2 = \left(\frac{\partial G}{\partial n_2}\right)_{n^1} = \Phi(G_2) + \frac{\partial \Phi(G)}{\partial \ln\ n_2} = \Phi(G_2) + \frac{\partial \Phi(G_2)}{\partial c} \cdot \frac{\partial c}{\partial \ln\ n_2} \tag{12}$$

[2] The relationship does not hold at higher concentrations.

Now

$$c = \frac{1000\, d}{M_2 + \left[\frac{n_1}{n_2} M_1\right]} \tag{13}$$

Eliminating d between equations 4 and 13 and rearranging terms gives

$$\Phi(V_2) = \frac{1000}{c} - \frac{M_1}{d_1} \cdot \frac{n_1}{n_2} \tag{14}$$

Differentiating equation 14 with respect to ln n_2 and rearranging terms gives

$$\left(\frac{\partial c}{\partial \ln n_2}\right)_{n_1} = c\left[\frac{1000 - c\Phi(V_2)}{1000 + c^2 \frac{\partial \Phi(V_2)}{\partial c}}\right] \tag{15}$$

Combining equations 12 and 15 gives the desired result:

$$\overline{G}_2 = \Phi(G_2) + c\left[\frac{1000 - c\Phi(V_2)}{1000 + c^2 \frac{\partial \Phi(V_2)}{\partial c}}\right] \frac{\partial \Phi(G_2)}{\partial c} \tag{16}$$

Whence,[3]

$$\overline{V}_2 = \Phi(V_2) + c\left[\frac{1000 - c\Phi(V_2)}{1000 + c^2 \frac{\partial \Phi(V_2)}{\partial c}}\right] \frac{\partial \Phi(V_2)}{\partial c} \tag{16'}$$

If Φ is expressed as a function of $c^{\frac{1}{2}}$ instead of c, equation 16 becomes

$$\overline{G}_2 = \Phi(G_2) + c^{\frac{1}{2}}\left[\frac{1000 - c\Phi(V_2)}{2000 + c^{3/2} \frac{\partial \Phi(V_2)}{\partial c^{\frac{1}{2}}}}\right] \frac{\partial \Phi(G_2)}{\partial c^{\frac{1}{2}}} \tag{17}$$

and

$$\overline{V}_2 = \Phi(V_2) + c^{\frac{1}{2}}\left[\frac{1000 - c\Phi(V_2)}{2000 + c^{3/2} \frac{\partial \Phi(V_2)}{\partial c^{\frac{1}{2}}}}\right] \frac{\partial \Phi(V_2)}{\partial c^{\frac{1}{2}}} \tag{17'}$$

This equation is perfectly general, and does not impose any particular functional relation on Φ and $c^{\frac{1}{2}}$. In the particular case where, as with most

[3] This equation was given by Geffcken (reference 2, equation 4). He discussed the relationship between Φ (V_2) and $\overline{V}_2$ in the dilute solution, but did not use this equation in actual calculation of values of $\overline{V}_2$.

electrolytes, $\Phi(G_2)$ and $\Phi(V_2)$ are linear functions of $c^{\frac{1}{2}}$, equation 17 can be further simplified to

$$\bar{G}_2 = \Phi^0(G_2) + \left[\frac{3000 - c\Phi^0(V_2)}{2000 + c^{3/2}\dfrac{\partial\Phi(V_2)}{\partial c^{\frac{1}{2}}}}\right]\frac{\partial\Phi(G_2)}{\partial c^{\frac{1}{2}}}\,c^{\frac{1}{2}} \tag{18}$$

If we are concerned with V_2, this equation becomes

$$\bar{V}_2 = \Phi^0(V_2) + \left[\frac{3000 - c\Phi^0(V_2)}{2000 + c^{3/2}\dfrac{\partial\Phi(V_2)}{\partial c^{\frac{1}{2}}}}\right]\frac{\partial\Phi(V_2)}{\partial c^{\frac{1}{2}}}\,c^{\frac{1}{2}} \tag{18'}$$

At infinite dilution,

$$\bar{G}_2^0 = \Phi^0(G_2)$$

At low concentrations, $c\Phi^0(V_2)$ and $c^{\frac{1}{2}}\dfrac{\partial\Phi(V_2)}{\partial c^{\frac{1}{2}}}$ are small compared with 3000 and 2000, respectively, and, as Geffcken pointed out,

$$\bar{V}_2 = \Phi^0(V_2) + 3/2\,\frac{\partial\Phi(V_2)}{\partial c^{\frac{1}{2}}}\,c^{\frac{1}{2}} \tag{19}$$

The limiting form of the equation at low concentration is similar to that developed by Randall and Rossini (9) for calculating the partial from the apparent molal heat capacity expressed as a function of the square root of the molality, namely,

$$\bar{C}_{p_2} = \Phi^0(C_{p_2}) + 3/2\,\frac{\partial\Phi(C_{p_2})}{\partial m^{\frac{1}{2}}}\,m^{\frac{1}{2}}$$

WEIGHT AND VOLUME CONCENTRATION

Plots against $c^{\frac{1}{2}}$ do not differ very much from those against $m^{\frac{1}{2}}$ at very low concentrations, since at the limit m is proportional to c. However, the difference may become appreciable at higher concentration. In general, rearranging equation 5 gives the relationship between c and m, namely[4]

$$\frac{c}{m} = d_1\left[1 - \frac{c\Phi(V_2)}{1000}\right] \tag{20}$$

c and m may be almost identical if $\Phi(V_2)$ is small or negative; or very different, if Φ is large. To illustrate this strikingly specific character of c/m we have chosen two univalent electrolytes as different as possible,

[4] The ratio is given by Geffcken (2) without the d_1. c and m are proportional and *not* equal, although the difference is small.

namely, lithium hydroxide and cesium iodide. The corresponding equations for $\Phi(V_2)$ are[5]

$$\Phi(V_2) = -6.00 + 3.00c^{\frac{1}{2}}$$

$$\Phi(V_2) = 47.9 + 1.47c^{\frac{1}{2}}$$

The values of c/m and $c^{\frac{1}{2}}/m^{\frac{1}{2}}$ calculated from equation 20 are given in table 1 at several values of $c^{\frac{1}{2}}$ and are plotted in figure 2.

TABLE 1

Values of c/m and $c^{\frac{1}{2}}/m^{\frac{1}{2}}$ calculated from equation 20

$c^{\frac{1}{2}}$	LiOH		CsI	
	c/m	$c^{\frac{1}{2}}/m^{\frac{1}{2}}$	c/m	$c^{\frac{1}{2}}/m^{\frac{1}{2}}$
0.0	0.9971	0.9985	0.9971	0.9985
0.5	0.9982	0.9991	0.9849	0.9924
1.0	1.0001	1.0000	0.9478	0.9736
1.5	1.0005	1.0002	0.8847	0.9406
2.0	0.9971	0.9985	0.7943	0.8800

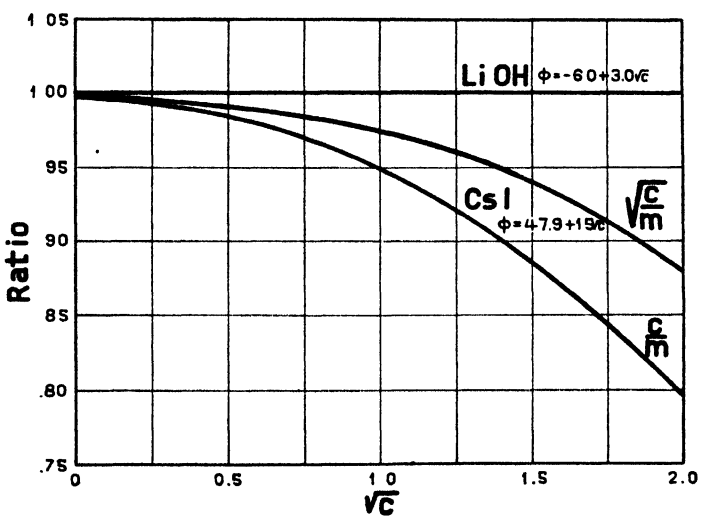

FIG. 2. DEPENDENCE OF c/m RATIO ON $\Phi(V_2)$

CALCULATION OF $\overline{V}_2$

As an application of equation 18′ we have taken the case of calcium chloride which was previously mentioned. The equation for the partial molal volume is

$$\overline{V}_2 = 18.25 + \left[\frac{3000 - 18.25c}{333.89 + c^{3/2}}\right] c^{\frac{1}{2}}$$

[5] The first was calculated from the density data of the International Critical Tables, 1st edition, Vol. III, p. 76; the second was taken from Geffcken (2).

The graph of this function is included in figure 1. Notice that $\overline{V}_2$ is nearly linear up to about 1 c. It is only above this concentration that the curve for $\overline{V}_2$ deviates appreciably from the dotted line which represents the limiting slope of the tangent.

In order to test the more general case to which equation 17′ is applicable we have studied the very precise specific volume data for ammonium nitrate solutions from 0.1 to 11 c at 25°C. which were obtained by Adams and Gibson (1). These particular data were chosen because the authors had made very careful computations on a *weight* basis with which we

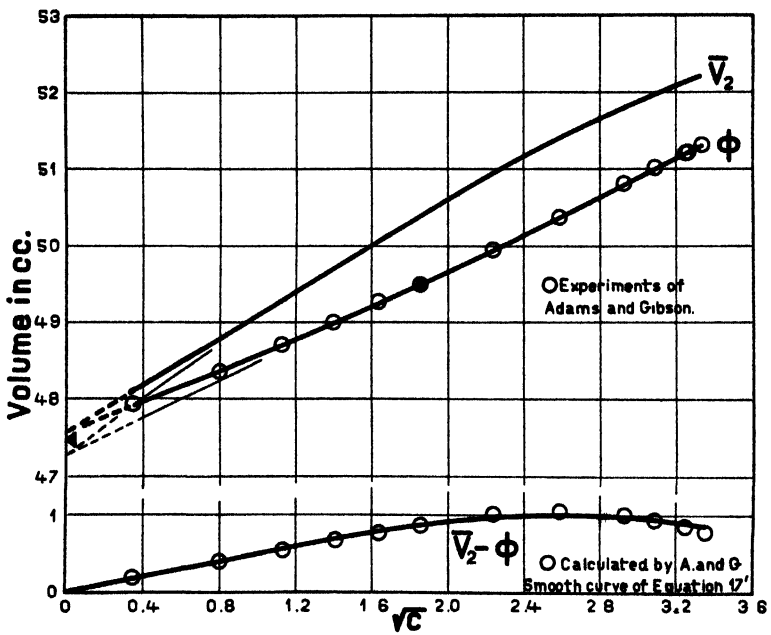

FIG. 3. AMMONIUM NITRATE AT 25°C.

could compare the results obtained from our equation. Moreover, in this case $\Phi(V_2)$ is large, so that the weight and volume scales diverge sharply at high concentration. We calculated values of $\Phi(V_2)$ from their data at fourteen points and found that they could be represented fairly well by the linear equation

$$\Phi = 47.280 + 1.2049c^{\frac{1}{2}}$$

However, appreciably better agreement was given by a second order equation in $c^{\frac{1}{2}}$, namely,

$$\Phi = 47.558 + 0.966c^{\frac{1}{2}} + 0.0474c$$

The average deviation in d calculated from the linear equation is 4.6×10^{-5} and from the quadratic curve 3.2×10^{-5}. The improved agreement

was particularly noticeable in the lower concentrations, and for this reason the extrapolation to zero concentration is much better with the quadratic equation. This is shown by the heavy line in figure 3. The lighter line represents the linear equation which extrapolates to an appreciably lower point. The two curves are practically identical above about 0.25 c.

From the second order equation for Φ we calculated the corresponding equation for d, of the form indicated by equation 11′, namely:

$$d = 0.997077 + 0.032628c - 9.63 \times 10^{-4}\, c^{\frac{3}{2}} - 4.73 \times 10^{-5}\, c^2$$

In calculating the partial molal volume, equation 17′ is changed to the form

$$\overline{V}_2 - \Phi(V_2) = \left[\frac{1000 - c\Phi(V_2)}{2000 + \dfrac{\partial\Phi(V_2)}{\partial c^{1/2}}\, c^{3/2}}\right] c^{\frac{1}{2}}$$

where

$$\frac{\partial\Phi(V_2)}{\partial c^{\frac{1}{2}}} = 0.966 + 0.948c^{\frac{1}{2}}$$

Our equation for $\overline{V}_2 - \Phi(V_2)$ is plotted at the bottom of figure 3. The equation for $\overline{V}_2$ is likewise included. Calculations from the linear and quadratic equations for Φ differ appreciably only below 0.25 c.

Adams and Gibson calculated φ (apparent volume per gram) and $\overline{V}_2$ (partial volume per gram). Plotting φ against the square root of the *weight fraction*, x_2, two equations were required to cover the whole range of concentration, namely:

$$\varphi = 0.59318 + 0.049161x_2^{\frac{1}{2}} \qquad (0 < x_2 < 0.10)$$
$$\varphi = 0.594118 + 0.043431x_2^{\frac{1}{2}} + 0.020524x_2^{\frac{3}{2}} \qquad (x_2 > 0.10)$$

They used the first equation in extrapolating to zero concentration. Our *molal* properties, $\Phi(V_2)$ and $\overline{V}_2$ are obtained by multiplying their values by the molecular weight (80.047). Their extrapolated value for $\Phi^0(V_2)$, indicated by the black triangle in figure 3, lies between our values extrapolated by the quadratic and linear equations. It is considerably nearer the former and agrees very well with our conclusions.

They calculated the partial volume by substituting in the equation

$$\bar{v}_2 = x_1x_2\frac{\partial\varphi}{\partial x_2} + \varphi$$

They evaluated the tangent $\dfrac{\partial\varphi}{\partial x_2}$ by tabular difference plots of φ and also checked the values of $2\bar{v}_2$ analytically from their interpolation equations.

A comparison of the results obtained by the weight and volume plots,

given in table 2, illustrates the extremely good agreement in almost all cases. In figure 3, the values of Adams and Gibson for $\overline{V}_2 - \Phi(V_2)$ are indicated by circles on the plot of our equation. The only appreciable deviations are shown at the two highest concentrations.

In comparing the two different methods of calculation the volume concentration plot is simpler, since one equation will cover the whole range of concentration. The weight fraction method requires *two* equations with different values for φ^0 as well as for the coefficient of $x_2^{\frac{1}{2}}$. Moreover, the volume plot smoothes the $\overline{V}_2$ curve in accordance with our present knowl-

TABLE 2

Ammonium nitrate at 25°C.—Comparison of methods

x_2	c	Φ (Gucker)	$10^3 \Delta \Phi$ = "obsd." − calcd.*	$\overline{V}_2 - \Phi$ (Gucker)	$\overline{V}_2 - \Phi$ (A.&G.)	$10^2 \Delta$ † (G − A.&G.)	$\overline{V}_2$ (Gucker)	$10^2 \Delta \overline{V}_2$ (G − A. & G.)
0.00	0.0	47.558	(−80)	0.00	0.00	0	47.56	8
0.01	0.125	47.906	−30	0.18	0.19	−1	48.08	1
0.05	0.635	48.358	−6	0.40	0.40	0	48.76	1
0.10	1.297	48.720	6	0.57	0.55	2	49.29	1
0.15	1.984	49.013	−7	0.70	0.68	2	49.71	2
0.20	2.700	49.273	−7	0.80	0.78	2	50.07	2
0.25	3.444	49.514	−13	0.88	0.87	1	50.39	2
0.35	5.024	49.961	−5	0.98	1.01	−3	50.94	−3
0.45	6.733	50.384	6	1.03	1.05	−2	51.41	−3
0.55	8.584	50.795	11	1.01	1.01	0	51.80	−1
0.60	9.567	50.999	10	0.98	0.95	3	51.98	2
0.65	10.590	51.204	−1	0.93	0.86	7	52.13	7
0.68	11.224	51.326	−11	0.89	0.79	10	52.22	11
						Av. = 3		Av. = 3

* "obsd." values were slightly corrected to even concentrations by Adams and Gibson. Calcd. values from our equation.

† $\Delta = (\overline{V}_2 - \Phi)$ (G) $- (\overline{V}_2 - \Phi)$ (A.&G.)

edge of simple functional relationships. The advantage of using a function which has theoretical justification rather than an empirical equation is particularly evident in the extrapolation to zero concentration. Redlich and Rosenfeld (11) illustrate strikingly the difference between a linear plot of $\overline{V}_2$ against $c^{\frac{1}{2}}$ and the fourth order empirical equation of La Mer and Gronwall, which passes through the same points and yet extrapolates to a very different value.

SUMMARY

We have described a simple method of calculating the apparent molal volume, $\Phi(V_2)$, as a function of $c^{\frac{1}{2}}$, which is shown to give the same results as the usual more laborious method.

We have compared volume and weight concentration. The ratio c/m is a specific property of the individual solute which depends on $\Phi(V_2)$ and may vary from 1 to less than 0.8.

We have developed a general equation for calculating any partial molal solute quantity, $\overline{G}_2$, from the corresponding apparent property $\Phi(G_2)$ as a function of c, and a special equation applicable when Φ is a linear function of $c^{\frac{1}{2}}$. Since many apparent molal properties of most electrolytes and some non-electrolytes show such a linear relationship, this equation has a very wide applicability.

We have shown the application of these equations in calculating partial molal volumes. In the case of ammonium nitrate we have compared our values of $\overline{V}_2$ calculated from a single equation for $\Phi(V_2)$ with those which Adams and Gibson calculated from two weight fraction plots. Our results are in substantial agreement with theirs, but theory and numerical simplicity seem to favor the volume concentration method.

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A NOTE ON THE COMPUTATION OF THE PARTIAL VOLUMES OF THE COMPONENTS IN AQUEOUS SOLUTIONS

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Certain advantages in convenience and accuracy arising from the use of volume concentrations rather than weight concentrations in the computation of those properties of phases of variable composition which depend on slopes, such as the partial volumes of the components, have been emphasized by Gucker in a recent article (6). Indeed, it appears that the apparent volume of the solute is more closely a linear function of the square root of the volume concentration than of the square root of the weight concentration. The formula for calculating the partial or partial molal volumes of the solute from volume concentration data is, it must be admitted (4), rather clumsy. If, however, one computes the partial volume of the *solvent* directly from the density data, one finds that the formulas involved are extremely simple and seem to furnish perhaps one of the most elegant ways of calculating partial or partial molal volumes. The object of this note is to call attention to the equation for computing the partial volumes of the solvent from density–volume concentration data and to apply the equation to data on solutions of sodium chloride, sodium sulfate, potassium chloride, potassium iodide, and lithium nitrate.

The symbols used are as follows:

V = Total volume of phase containing m_1 grams of solvent and m_2 grams of solute.

v = Specific volume of the phase.

v_w = Specific volume of pure solvent.

v_1 = Partial volume (per gram) of solvent in a given phase.

v_2 = Partial volume (per gram) of solute in a given phase.

ϕ_2 = Apparent volume (per gram) of solute in a given phase.

x_1 and x_2 = Weight fractions of solvent and solute, respectively.

ρ_w = Density of pure solvent.

ρ = Density of phase.

$\rho_1 = \dfrac{1}{v_1}$ = Fictive density[1] of the solvent in a given phase.

[1] The *fictive density* of a component in a solution may be defined as the reciprocal of its partial volume. The term *fictive volume* is frequently used for the quantity which is called the *partial volume* in this paper. The term *partial volume* is preferred as it emphasizes the definition and is closely allied to the partial molal volume.

c_2 = Concentration of solute in grams per cubic centimeter of solution = ρx_2.

By definition

$$V = m_1 v_w + m_2 \phi_2 \tag{1}$$

and

$$v_1 = \left(\frac{dV}{dm_1}\right)_{P, T, m_2} \tag{2}$$

Hence

$$\left(\frac{d\phi_2}{dm_1}\right)_{P, T, m_2} = \frac{v_1 - v_w}{m_2} \tag{3}$$

As

$$c_2 = \frac{m_2}{V}$$

it follows that

$$v_1 = -\frac{m_2}{c_2}\frac{dc_2}{dm_1} \tag{4}$$

From equations 3 and 4 it may readily be shown that

$$v_1 = -\frac{1}{c_2^2}\frac{dc_2}{d\phi_2}(v_1 - v_w) \tag{5}$$

or

$$v_1 = \frac{v_w}{1 + c_2^2 \dfrac{d\phi_2}{dc_2}} \tag{6}$$

If the variable be changed from c_2 to $c_2^{\frac{1}{2}}$, we obtain equations 7 and 8:

$$v_1 = \frac{v_w}{1 + \frac{1}{2} c_2^{\frac{3}{2}} \dfrac{d\phi_2}{dc_2^{\frac{1}{2}}}} \tag{7}$$

or

$$\rho_1 = \rho_w + \tfrac{1}{2} c_2^{\frac{3}{2}} \frac{d\phi_2}{dc_2^{\frac{1}{2}}} \rho_w \tag{8}$$

Now Gucker has shown that if

$$f = \frac{\rho_w - \rho}{c_2} \tag{9}$$

then

$$\rho_w \phi_2 = f + 1 \tag{10}$$

and that

$$\rho_w \frac{d\phi_2}{dc_2^{\frac{1}{2}}} = \frac{df}{dc_2^{\frac{1}{2}}} \tag{11}$$

Thus, as a final expression for the fictive density of the solvent in a phase we have equation 12:

$$\rho_1 = \rho_w + \tfrac{1}{2} c_2^{\frac{3}{2}} \cdot \frac{df}{dc_2^{\frac{1}{2}}} \tag{12}$$

Equations 12 and 17′ are particularly applicable to gaseous solutions where the data are frequently expressed in tables with the density as entry and the concentration in mass per unit volume as argument.

As the chief value of equation 12 lies in the presumption that ϕ_2 or f is a linear function of the square root of the volume concentration, it was considered desirable to determine by the method of least squares how closely equation 13 represents good density data over the entire range.

$$-f = \frac{\rho - \rho_w}{c_2} = a + bc_2^{\frac{1}{2}} \tag{13}$$

$$\rho - \rho_w = ac_2 + bc_2^{\frac{3}{2}} \tag{14}$$

It is a relatively simple matter to determine the coefficients a and b in equation 13 by the method of least squares, as

$$a = -\frac{\begin{vmatrix} \sum f & \sum c_2^{\frac{1}{2}} \\ \sum fc_2^{\frac{1}{2}} & \sum c_2 \end{vmatrix}}{\begin{vmatrix} n & \sum c_2^{\frac{1}{2}} \\ \sum c_2^{\frac{1}{2}} & \sum c_2 \end{vmatrix}} \quad \text{and} \quad b = -\frac{\begin{vmatrix} n & \sum f \\ \sum c_2^{\frac{1}{2}} & \sum fc_2^{\frac{1}{2}} \end{vmatrix}}{\begin{vmatrix} n & \sum c_2^{\frac{1}{2}} \\ \sum c_2^{\frac{1}{2}} & \sum c_2 \end{vmatrix}} \tag{15}$$

where n is the number of terms in the table of density and concentration. However, at low concentrations f is the ratio of two very small quantities, and small errors in density produce large changes in f and too much weight may be given to these deviations, which are within the allowable error of experiment. Equation 14 avoids this difficulty but necessitates the summation of several more powers of the volume concentration. The least-square solution of equation 14 gives a and b as follows:

$$a = -\frac{\begin{vmatrix} \sum fc_2 & \sum c_2^{\frac{1}{2}} \\ \sum fc_2^{\frac{3}{2}} & \sum c_2^{3} \end{vmatrix}}{\begin{vmatrix} \sum c_2^{2} & \sum c_2^{\frac{3}{2}} \\ \sum c_2^{\frac{5}{2}} & \sum c_2^{3} \end{vmatrix}} \quad b = -\frac{\begin{vmatrix} \sum c_2^{2} & \sum fc_2 \\ \sum c_2^{\frac{5}{2}} & \sum fc_2^{\frac{3}{2}} \end{vmatrix}}{\begin{vmatrix} \sum c_2^{2} & \sum c_2^{\frac{3}{2}} \\ \sum c_2^{\frac{5}{2}} & \sum c_2^{3} \end{vmatrix}} \tag{16}$$

In this paper a and b for the sodium sulfate solutions were evaluated by the application of equation 16 over the whole range of concentration, but for the solutions of the other salts a and b were computed from equation 15, applied over the range from $c_2 = 0.05$ (approximately) to the highest concentration.

The results of the computations are given in tables 1 to 5. At the head of each table equation 13 or 14, with the appropriate values of a and b, is given and the tables themselves show how well the equation fits the data and the values of the partial volumes of the components computed by the equations:

$$\frac{1}{v_1} = \rho_1 = \rho_w + \frac{b}{2} c_2^{\frac{3}{2}} \tag{12'}$$

and

$$v_2 = \frac{v}{x_2} - \frac{x_1 v_1}{x_2} \tag{17}$$

which may also be written in the convenient form,

$$v_2 = v_1 \left(1 - \frac{\rho - \rho_1}{c_2}\right) \tag{17'}$$

The partial molal volume of a component may be obtained by multiplying its partial volume by its molecular weight.

The data on which the results in table 1 are based are those of Hall (7) and are of a high order of accuracy.

The least-square residuals in column 4, however, show that equation 13 does not represent the results within the error of experiment. The fit is good and, as an interpolation formula, equation 14 leaves little to be desired, but as a means of determining slopes it leaves room for uncertainty. With sodium chloride solutions some idea of the uncertainty in the slopes may be had from a comparison of the partial volumes of the salt as calculated by equations 12′ and 17, and those computed very carefully by Adams (1) with the aid of an empirical cubic equation and a deviation curve. This comparison is made in the last two columns of table 1.

In the 5 per cent solution and in the 25 per cent solution the agreement is poor, but in the intermediate solutions the two methods give results which are in excellent accord.

Table 2 illustrates the result of fitting equation 14 by the method of least squares to Gibson's (5) results for the densities of solutions of sodium sulfate, which were measured with considerable care. The least-square

TABLE 1

Computations for solutions of sodium chloride at 25°C.

$(\rho - \rho_w)/c_2 = 0.72122 - 0.15345c_2^{\frac{1}{2}}$

x_2	c_2	$(\rho - \rho_w)$calcd.	ρobsd $-$ ρcalcd. $\times 10^4$	v_2	v_2 (Adams)
0.0	0.0	0	0	0 2796	0 2914
0.02	0 02022	0.01414	−4	0 3145	—
0.03	0 03055	0 02121	−4	0.3213	—
0.05	0.05163	0.03544	−2	0.3318	0.3304
0.10	0.10688	0.07172	4	0.3537	0.3539
0.15	0 16596	0 10932	2	0.3716	0.3725
0.20	0.22909	0 14840	−4	0 3870	0.3873
0.25	0.29654	0.18909	−1	0 4002	0.3991

TABLE 2

Computations for solutions of sodium sulfate at 25°C.

$(\rho - \rho_w) = 0.92212c_2 - 0.23567c_2^{\frac{3}{2}}$

x_2	c_2	$(\rho - \rho_w)$calcd.	ρobsd $-$ ρcalcd $\times 10^4$	v_1	v_2	v_2 (1926)
0 0				1 00293	0 0781	0 0860
0.01	0.01006	0 009039	$-1._4$	1 00281	0.1151	0 1144
0.02	0.02030	0.018039	-2_2	1.00259	0 1296	0 1288
0.03	0 03072	0 027061	-2_1	1.00229	0 1409	0.1394
0.05	0.05212	0.045254	-0_1	1.00152	0 1588	0.1578
0.10	0.10890	0 091954	1_2	0.99869	0 1942	0 1940
0.15	0.17068	0 140770	$3._1$	0 99464	0 2225	0.2226
0.20	0 23781	0.191957	$-0._2$	0 98937	0.2476	0.2478
0 25	0.31069	0.245681	$-0._4$	0.98282	0.2701	0 2698
0.28	0.35736	0.279181	$1._8$	0.97824	0 2829	0.2824

residuals are small, but are outside the experimental error and show a distinct curvature.

The partial volumes of the salt, as computed directly from equations 12′ and 17, the residuals being neglected, are compared with the values of the partial volumes as calculated by Gibson from several empirical equations and deviation curves. The agreement is good, except at zero concentration where, it is believed, all weight should be given to the formula involving

the square root of the concentration. Sodium sulfate changes the density of water very markedly and the partial volumes of the salt increase rapidly with the concentration; it is remarkable, then, that a two-constant equation such as equation 14 should represent the density as a function of the concentration so precisely.

Apparently the best data on the densities of potassium chloride solutions are those of Baxter and Wallace (2) and of Geffcken (3). In the determination of the coefficients a and b in equation 13 all the points except the first three of Baxter and Wallace were used. In general the equation fits the data well, but there is a pronounced departure at the highest concentra-

TABLE 3

Computations for solutions of potassium chloride at 25°C.

$(\rho - \rho_w)/c_2 = 0.64611 - 0.1159c_2^{\frac{1}{2}}$

c_2	$(\rho - \rho_w)_{calcd.}$	$\rho_{obsd.} - \rho_{calcd.} \times 10^5$	v_1	v_2	
0.01235	0.00782	0	1.00285	0.374_4	Baxter and Wallace
0.02023	0.01274	−2	1.00276	0.380_1	
0.02491	0.01564	−1	1.00270	0.382_8	
0.04988	0.03094	−5	1.00228	0.394_5	
0.06850	0.04218	1	1.00189	0.400_1	
0.12447	0.07533	2	1.00038	0.415_2	
0.17094	0.10226	1	0.99883	0.422_1	
0.24964	0.14684	−1	0.99571	0.438_9	
0.10633	0.06468	8	1.00091	0.410_3	Geffcken
0.15397	0.09248	0	0.99942	0.421_9	
0.20636	0.12247	−2	0.99750	0.431_8	
0.28836	0.16837	−11	0.99399	0.444_9	
0.28926	0.16887	−7	0.99395	0.444_9	

tions. The residual of 5×10^{-5} in Baxter and Wallace's data, and the residuals of 11×10^{-5} and 7×10^{-5} in Geffcken's results for the most concentrated solutions seem to indicate inconsistencies in the experimental work. The partial volumes of water and of potassium chloride in the various solutions were computed by equations 12 and 17′ and are given in the fourth and fifth columns of table 3. The residuals were neglected in these calculations, and indeed the experimental results hardly warrant the use of a deviation curve.

Being interested in the effect of pressure on the solubility of potassium iodide, we examined the partial volumes of this salt in aqueous solutions. The results are given in table 4. The data are those of Baxter and Wallace (2), and of Shibata and Hölemann (9), the latter's results being marked with an asterisk. The equation at the head of the table was obtained by

the method of least squares using $c_2^{\frac{1}{2}}$ as argument (equation 13). It is obvious that the two sets of data are not consistent and the passing of linear equations through both sets separately indicated that those of Baxter and Wallace were smoother than those of Shibata and Hölemann. It is also obvious that the linear relationship does not hold over the whole concentration range for this salt—the highest points fall off the straight

TABLE 4

Computations for solutions of potassium iodide at 25°C.

$(\rho - \rho_w)/c_2 = 0.72825 - 0.02403c_2^{\frac{1}{2}}$

c_2	$(\rho - \rho_w)_{calcd.}$	$\rho_{obsd} - \rho_{calcd.} \times 10^5$	v_1	v_2
0.04571	0.03305	−1	1.00281	0.280_7
0.09185	0.06622	−1	1.00259	$0\ 283_7$
0.16686*	0.11988	1*	1.00209	0.287_2
0.18466	0.13257	−2	1.00196	0.288_0
0.27000*	0.19326	6*	1.00121	0.290_8
0.35477*	0.25328	10*	1.00036	0.293_1
0.44465*	0.31669	15*	0.99932	0.295_4
0.46084	0.32809	0	0.99912	(0.296_0)
0.64032*	0.45400	8*	0.99670	$(0\ 299_6)$
0.92425	0.65173	−47	0.99268	(0.304_3)

[1] Data of Shibata and Hölemann.

TABLE 5

Computations for solutions of lithium nitrate at 25°C.

$(\rho - \rho_w)/c_2 = 0.58035 - 0.04534c_2^{\frac{1}{2}}$

m	c_2	$(\rho - \rho_w)_{calcd.}$	$\rho_{obsd} - \rho_{calcd.} \times 10^5$
1.0339	0.06895	0.03919	−10
2.1115	0.13662	0.07700	100
3.3106	0.20685	0.11578	18
4.5706	0.27579	0.15349	38
5.9276	0.34474	0.19089	29
7.3940	0.41368	0.22802	6
8.9836	0.48262	0.26489	−13
10.7055	0.55157	0.30153	26
11.8331	0.59318	0.32354	−37
12.8639	0.62934	0.34260	−72

line. Unfortunately, the inconsistencies between the two sets of experimental results do not admit of an accurate estimate of this curvature.

The partial volumes, v_1 and v_2, in table 4 were computed directly from the equation

$$\rho - \rho_w = 0.72818c_2 - 0.02429c_2^{\frac{3}{2}}$$

which, according to the least-square criterion, is the best straight line which may be passed through Baxter and Wallace's results. No attempt

was made to take account of the deviations from the above equation and in consequence the results at the higher concentration are not to be taken as final.

Pearce and Nelson (8) published a very complete series of densities of solutions of lithium nitrate over the whole concentration range at 25°C. Equation 13 was fitted to these data by the method of least squares and the results are recorded in table 5. The least-square residuals are very large and indicate that $(\rho - \rho_w)/c_2$ is by no means a linear function of the square root of the volume concentration. An analysis also reveals that the results are somewhat erratic; indeed the density of the 2.115 molal solution was so far off that it was omitted from the least-square calculation. Unless the results of Pearce and Nelson are very much in error it appears that the linear equation is of little use in the computation of partial volumes in lithium nitrate solutions.

It seems significant that the greater the contraction in volume produced by a salt on forming an aqueous solution, the better does the linear function of $c_2^{\frac{1}{2}}$ represent the apparent volume of the salt.

SUMMARY

The computation of the partial or partial molal volumes of the components in a solution is always a laborious process if the best use is to be made of the experimental data. The use of the volume concentration and Gucker's function f, together with equations 12 and 17 or 17′ in this paper, furnishes a relatively simple method of calculation, which in the case of many aqueous salt solutions (four out of the five examined here) yields values of the partial volume of the salt which are trustworthy to within one per cent, and, if a deviation curve is used, even higher accuracy may be obtained. If, however, the plot of f against the square root of the volume concentration is so strongly curved that higher powers of $c_2^{\frac{1}{2}}$ are to be introduced into the analytical expression, or if the desired accuracy of the computation requires the introduction of higher powers of $c_2^{\frac{1}{2}}$, the virtue of the volume concentration as an argument is lost and either weight or volume concentrations may equally well be used. The method of least squares is particularly recommended in the fitting of the empirical equations 13 and 14 to the experimental data.

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THE TEMPERATURE COEFFICIENT OF THE RATE OF COMBINATION OF HYDROGEN AND OXYGEN UNDER ALPHA RADIATION

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Although this reaction has been extensively investigated under many conditions for various purposes (5), the temperature range of the alpha-ray reaction has never been extended above 130°C. nor below −80°C. The investigations of the thermal reaction by Hinshelwood and Thompson (2) and of the photochemical reaction by Kistiakowski (3), both at higher temperatures, make it appear desirable to extend the temperature limits of the alpha-ray reaction in both directions. Owing to the nature of the reactants and to the absence of the reverse reaction, the decomposition of water vapor by alpha rays, the reaction lends itself admirably to such a purpose.

The objects of the study are to contribute to the knowledge of the reaction mechanism, especially to the transition from a constant quantized reaction with no temperature coefficient at lower temperature to a chain reaction with about the same temperature coefficient as the photochemical reaction at higher temperatures.

Incidentally the sensitization or catalytic effect of ions of water vapor has been discovered and found to be 100 per cent efficient.

GENERAL PROCEDURE

The manometer method of following the course of the reaction has been used in all except one experiment. The two methods of using radon, (1) by mixing directly with the reactants, and (2) by confining it in a thin alpha-ray bulb at the center of the reaction sphere, have been employed. Reaction spheres of Pyrex glass were used. Both static and circulating systems were employed with various conditions as to extent and temperature of the dead arm kept at lower temperature for condensation of water vapor, since it was not feasible to employ an internal drying agent at high temperature. Electrolytic gas was generated from barium hydroxide solution between platinum electrodes and stored in a vessel without stop-

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cocks. Figure 1 shows the apparatus used in the circulation method, in which I is the reaction sphere containing an alpha-ray bulb at its center in the electrical furnace H at a controlled temperature, E is the all-glass magnetic circulating pump of simple design (8), and J is a heating coil to raise the temperature of a small platinum catalyst to produce initial saturation with water vapor. G is a liquid air trap sometimes used to remove the water vapor from the circulating mixture.

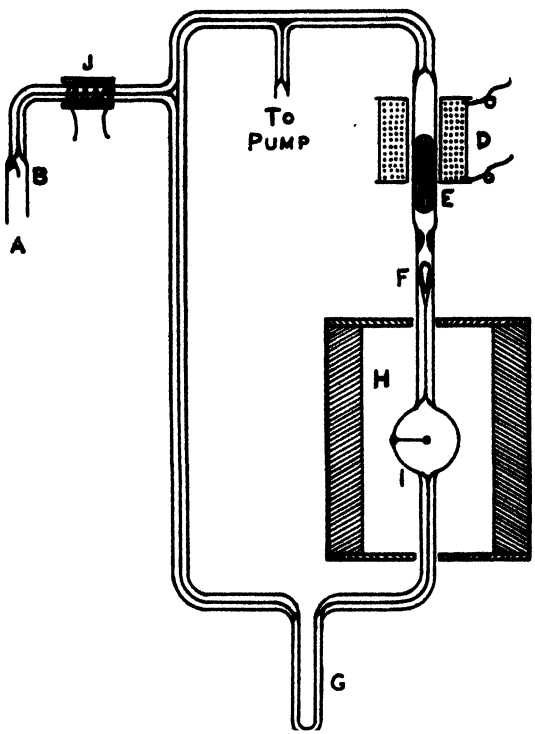

FIG. 1. APPARATUS USED IN THE CIRCULATION METHOD

Radon purified by the method of Livingston (7) is introduced either into the alpha-ray bulb of figure 1, the stem of which is then sealed and closed as far as the bulb (by a technique to be described later), or is introduced into the tube shown in the breaker M of figure 2, from which it is introduced into sphere G in the static method after breaking *in vacuo*.

TREATMENT OF DATA

The quantity of radon is initially measured by its gamma radiation and its decay is subsequently followed by the table of Kolowrat. The gas pressures (at constant volume) have all been corrected to 0°C. The

kinetic constant is calculated in the usual way (reference 5, p. 116) from the equation

$$\left(\frac{k\mu}{\lambda}\right)' = \text{const.} = \frac{\text{nat log}\,\dfrac{P_1}{P_2}}{E_0\,(e^{-\lambda t_1} - e^{-\lambda t_2})}$$

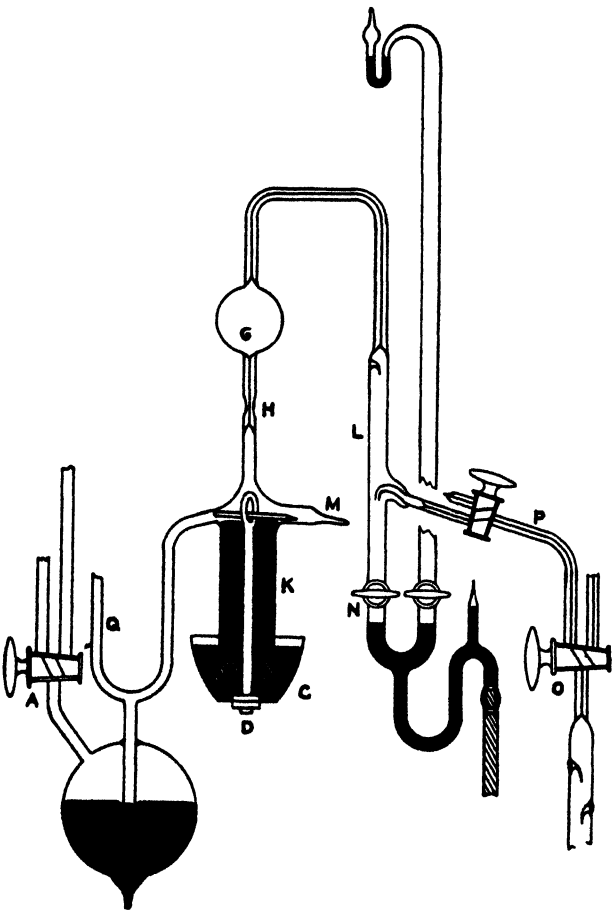

FIG. 2

From the values of $\left(\frac{k\mu}{\lambda}\right)'$ for each interval the number of molecules of hydrogen and oxygen reacting per ion pair is calculated and reported as $-M/N$, where N is the total number of ion pairs from O_2, H_2, or H_2O except in cases where ions of water vapor may be neglected. Comparison of yields under different conditions is therefore obtained by direct com-

parison of corresponding M/N values. It is assumed that the amount of ionization by alpha particles is unaffected by temperature at any temperature employed.

EFFECT OF WATER VAPOR

Duane and Scheuer (1) found that water vapor is not decomposed by alpha rays. On the other hand it is normally ionized and hence may possibly contribute to the forward reaction just as Lind and Bardwell (6) later found many foreign gas ions do in various reactions including the effects of ions of nitrogen, oxygen, and neon in water synthesis. Such an effect of water vapor in water synthesis would be "autocatalytic," increasing with increase of water vapor produced in the reaction itself. Such an effect has hitherto escaped observation because at ordinary temperature most of the water formed condenses out. An effect of H_2O^+ (or possibly H_2O^-) ions would be expected to become relatively more important at low pressures of electrolytic gas saturated with water vapor. But in the reactions at low pressure in the investigations of recoil atom effect (4) an internal drying agent was used so as to prevent any influence of water vapor on the recoil effect.

In the present experiments at higher temperatures, however, the water vapor concentration becomes sufficiently great to contribute materially to the ionization and also, as will be shown, to the reaction rate.

On going up in temperature a marked increase in $-M/N$ is observed, which may be due either to a true temperature effect or to the catalytic effect of water vapor ions or to both. The effect of water ions must be known or eliminated in order to evaluate the true temperature coefficient. Both methods have been used, to remove water vapor by the circulation method or to calculate the additional effect in the presence of water vapor and subtract it. Both lead to the same net result at a given temperature. Moreover the agreement confirms the 100 per cent efficiency of water vapor ions, which was assumed in making the subtractive correction.

Another accelerating effect, that of low pressure, which was first thought to exist, proved to be spurious upon more complete removal of water vapor and was due to the relatively enhanced effect of the latter at low pressures of reactants.

The practically complete elimination of water vapor (not extreme drying) leaves then only the true yield $-M/N$ which remains constant at 4.5[3] from $-180°$C. to ordinary temperature and then rises steadily to 20

[3] Throughout this paper the results are expressed in terms of $-M/N$, i.e., the number of molecules of hydrogen and of oxygen reacting per ion pair produced both in hydrogen and in oxygen ($-M_{H_2+O_2}/N_{H_2+O_2}$). In terms of water molecules formed the value is $2/3 \times 4.5 = 3$. This is lower than the earlier value 4, because the values of the average intensity of ionization obtained from the Mund equation are higher and hence N is higher and M/N is lower.

at 400°C.; between 400°C. and 500°C. the values were not reproducible owing to the thermal reaction; above 500°C. the reaction becomes explosive.

EXPERIMENTS AND CALCULATIONS IN STATIC SYSTEM

In the following tables are reported the observations and calculations of experiments under various conditions of temperature and of water removal.

The experiments in static systems above 100°C. were found quite useless in attempting to find the true temperature coefficient of reaction rate, because the slow rate of diffusion of water vapor from the reaction sphere out to room temperature produces a higher partial pressure of water vapor in the reaction sphere than is allowed for by simply applying the water vapor correction for the outside (lower) temperature. The application of cooling baths outside is ineffective in speedy removal of water vapor, since it is the rate of diffusion outward, not the rate of condensation after arriving there, which is the controlling factor. The apparent yield in water synthesis per ion pair continues to rise even at a constant higher temperature, which may be due either to an actual increase of rate due to accumulation of more water vapor (which seems improbable, beyond a certain limit, over the long periods of time that prevail toward the end of the reaction) or to the increasing importance of water vapor relative to the diminishing pressure of electrolytic gas, since both are ionized in proportion to their amounts present.

Table 1 will illustrate such a false rise of $-M/N$ at 275°C. due to this cause. P_0 = the pressure of reactants corrected to 0°C., after subtracting aqueous tension at the outside temperature. P_{eq} = the pressure of reactants at 0°C. increased by the ion equivalence[4] of the water vapor pressure.

As already explained, the large rise in $-M/N$ is spurious and caused by accumulating water vapor above equilibrium with the outside temperature, but owing to the uncertainty of its amount, correction cannot be made until the water concentration is known or eliminated.

One method of procedure which was adopted with fair success was to make a rate measurement at each temperature so as to obtain a value of M/N before enough water vapor had been produced or the reactants sufficiently diminished to influence the value of M/N. Such measurements were made at 25°, 75°, 125°, 160°, 199°C. The details are not reported but the results are given in figure 3 and agree with the results where water vapor is rigidly removed.

A second method consisted in employing an alpha-ray bulb (with com-

[4] It is P_{eq} which is substituted in the general kinetic equation to obtain the velocity constant $\left(\frac{k\mu}{\lambda}\right)'$ from which M/N is calculated in the usual way.

TABLE 1

Rate of combination at 275°C. with incomplete removal of water vapor

Volume of reaction sphere = 10.41 cm³. Diameter of reaction sphere = 2.708 cm. Initial radon = 0.1059 curie. Static system with radon mixed with $2H + O_2$

ELAPSED TIME		$e^{-\lambda t}$	P_s	P_{eq}	RECOIL ATOM CORRECTION	$\frac{(k\mu)'}{\lambda}$	$\frac{-M}{N}$	TEMPERATURE OF REACTION
days	*hours*							*degrees C.*
0	0	1.00000	367.8	400.8	—	—	—	—
0	22	0.8478	312.7	345.7	1.119	9.2	3.7	25
1	6.58	0.7955	289.5	322.5	1.137	12.5	4.9	25
1	20.42	0.7216	248.2	281.2	1.155	17.5	6.8	285
2	4.25	0.6758	215.3	248.3	1 180	25.7	9.8	275
2	20.92	0.5968	168.8	201.8	1 218	24.8	9.3	275
3	4.83	0.5620	142.4	175.4	1.268	38.1	13.9	275
3	10.25	0.5396	128.8	161.8	1.311	38.6	13.5	275
3	18.25	0.5082	112.0	145.0	1.351	32.5	11.2	275
4	4.92	0.4689	93.1	126.1	1.407	34.4	11.7	275
4	20.42	0.4174	62 7	100.2	1.520	42.2	13.7	275
5	2.92	0.3975	58.1	91.1	1.664	45.2	14.0	275
5	8.58	0.3814	46.5	79 5	1.797	79.9	23.8	275
5	21.83	0.3447	15.9	48 9	2.334	125.1	33.6	275
5	22.83	0.3421	11.1	44.1	4.019	375.1	87.5	275
5	23.83	0.3396	7.9	40.9	5.710	284.4	61.9	275

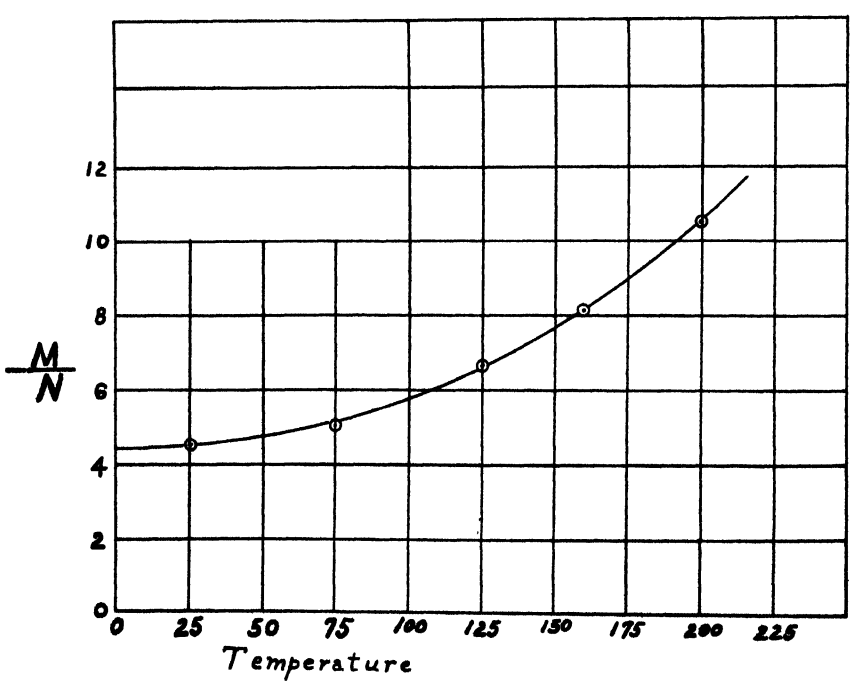

FIG. 3

pletely closed stem) mounted at the center of the reaction sphere. This permitted surrounding the entire sphere with liquid air or carbon dioxide mixture so as to freeze the water vapor on the walls as ice. This method is naturally limited to the low temperature measurements. When the bath is removed the water vapor produced at higher temperature causes an enhancement[5] in M/N as shown in table 2.

A special experiment was made to examine the value of M/N at −78°C. which was apparently higher than that either at 25° or −183°C. The results were: at 25°C., 4.4, 4.65; at −78°C., 5.1, 4.98, 4.61; at 25°C., 4.03. The

TABLE 2

Rate of synthesis at low temperatures in absence of water vapor compared to that in its presence at higher temperatures

Volume of reaction sphere = 14 cc. Radon in alpha-ray bulb = 0.100 curie

TIME ELAPSED		e^-	P_0	P_{eq}	$\frac{(k\mu)'}{\lambda}$	$\frac{-M}{N}$	TEMPERATURE
days	*hours*						*degrees C*
—	—	1.0000	446.0	482.0	—	—	—
	19.0	0 8672	415.0	451 0	5 00	4.42	25
1	19.5	0.7216	371 7	371.7*	7.58	6.56	−78
2	20 5	0.5982	340 4	340.4*	7.23	6.25	−78
3	19 5	0.5034	318.7	318.7*	6.95	6.00	−78
4	20.0	0.4190	304 6	340.6	4.81	—	—
5	19.5	0 3512	294 0	294.0*	5.22	4.52	−183
6	20.5	0.2912	285.8	285.8*	4.72	4.08	−183
7	19.5	0.2450	276.7	312.7	6.22	5.38	25
8	20.5	0.2039	241 9	277.9	35.0	30.3	353
9	20.5	0.1703	151.8	187.8	48.1	41.6	380
10	19 0	0.1439	141.6	177.6	21.2	18.4	290

* At these temperatures water froze on the sides of the vessel so that no water vapor is present in the path of the alpha particles.

results for −78°C. are lower than in table 2 but still somewhat higher than those for 25°C., for which no explanation has been offered.

EXPERIMENTS WITH CIRCULATING SYSTEM

It became evident that for the prompt and complete removal of water vapor the reactant gases should be circulated through an outside liquid air trap. This was accomplished by means of an all-glass pump and an alpha-ray bulb to prevent circulation of the radon. The results given in table 3 demonstrate the constancy of M/N at 175°C. under these conditions and

[5] That these enhanced values are not due alone to the higher temperature is evident when they are compared with those of corresponding temperatures in the absence of water vapor, as shown in table 4.

are to be contrasted with those of table 1 where water vapor was allowed to accumulate.

TABLE 3

Synthesis of water at 175°C. in absence of water vapor

Volume of reaction sphere = 12.150 cc. Volume of system outside oven = 8.104 cc. E_0 = 0.100 curie, in alpha-ray bulb. Circulation with all-glass pump

TIME ELAPSED		$e^{-\lambda t}$	P_0	P_{eq}	$\frac{(k\mu)'}{\lambda}$	$\frac{-M}{N}$	TEMPERATURE
days	*hours*						*degrees C.*
—	—	1.0000	159.6	192.6	—	—	—
—	18.75	0.8686	134.8	167.8	10.48	—	25
2	16.25	0.6176	110.6	143.6	6.21	4.5	25
2	17.67	0.6111	109.4	109.4*	—	—	—
2	23.25	0.5860	106.2	106.2*	11.97	8.7	175
3	20 75	0.4987	95.1	128.1	12.65	9.2	175
4	13.25	0.4407	87.1	120.1	11.13	8.0	175
4	24.67	0.4045	81.9	114.9	12.21	9.1	175
5	21.25	0.3467	74.9	107 9	10.81	7 4	175
6	22 33	0.2873	67.6	100.6	11 86	8.6	175
7	22.00	0.2405	65.1	95.1	12.02	8.9	173

TABLE 4

Synthesis of water at various temperatures in absence of water vapor

Volume of sphere = 14 cc. E_0 = 0.100 curie in alpha-ray bulb. Circulation by all-glass pump

TIME ELAPSED		$e^{-\lambda t}$	P_0	P_{eq}	$\frac{(k\mu)'}{\lambda}$	$\frac{-M}{N}$	TEMPERATURE
days	*hours*						*degrees C.*
—	—	1.0000	595.7	543.7	—	—	—
—	20	0.8608	557.1	502.9	5.6	4.5	25
1	17.5	0.7325	510.8	464.5	6.15		25
2	6.25	0.6657	461.6	414 1	17.2	13.2	300
2	17.75	0.6106	446 9	400.4	6.1	4.65	25
3	4.00	0.5655	434 1	374.3	15.0	11.45	300
3	20.00	0.5016	184.1	162.7	130.6	99.8	500
4	19.25	0.4213	148 7	133.7	24.4	18.6	350
4	19.75	0.4196	445.9	398.0	(1)		
5	18.75	0.3532	393.4	353.5	17.8	13.6	358
6	18.5	0.2956	326.7	292.1	33.15	25.14	404
7	18.5	0.2469	92 7	82.1	260.4	198.4	500

(1) More reaction gas added.

Circulation by thermal convection was also tried, but was found to give results less satisfactory than the foregoing. It only remained then to apply the circulation method at various temperatures. In each case the alpha-

TABLE 5

Synthesis at higher temperature in absence of water vapor

Volume of sphere = 14 cc. E_0 = 0.105 curie in alpha-ray bulb. Circulation by means of all-glass pump

TIME ELAPSED		$e^{-\lambda t}$	P_{c_0}	P_{eq}	$\frac{(k\mu)'}{\lambda}$	$\frac{-M}{N}$	TEMPERATURE
days	*hours*						*degrees C.*
—	—	1.0000	288.4	315.4	—	—	—
—	17.75	0.8751	276.8	301.8	3 0	4 6	25
1	19.0	0.7243	254.1	279 1	5.2		25
2	14.25	0.6269	220.6	245 6	14.3	13 4	400
3	17 75	0.5100	207 2	232 2	4 8	4 6	25
4	15.50	0.4333	142.6	167.6	43 2	40 2	480
5	21.75	0.3453	136.6	161.6	4 3	4.2	25
5	22 00	0 3447	226 2	251.2	(1)		
6	19 25	0.2939	208 0	233 0	15 1	14 0	284
7	16.25	0.2511	195 3	220.3	13 2	12 3	375
7	16 5	0 2506	286 0	311 0	(1)		
8	16 5	0 2093	119 0	144 0	188 0	175.0	525

(1) More reaction gas added.

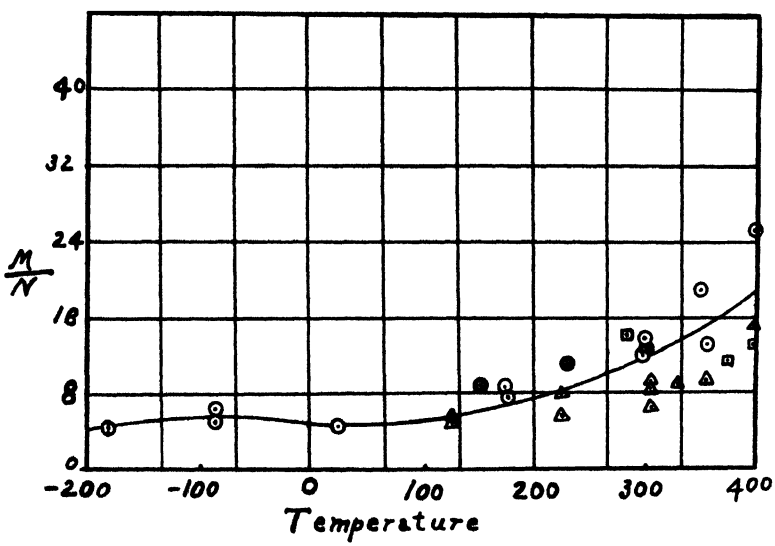

FIG. 4

ray bulb and reaction sphere are calibrated for ionization by means of reaction rate of electrolytic mixture at 25°C. The detailed results of two of these experiments at various temperatures are given in tables 4 and 5.

One experiment was carried out in a closed static system consisting of a

sphere and short connecting tube all enclosed at the reaction temperature 300°C. so as to test the complete correction for a known amount of water vapor. Assuming 100 per cent efficiency of the ions of water vapor gave the value $M/N = 14$, in good agreement with those of the circulating method, thus proving the rôle of water vapor ions and their 100 per cent efficiency in promoting synthesis.

In figure 4 are plotted the results of a number of experiments at temperatures ranging from −183°C. to 400°C. From this curve are calculated the temperature coefficients which are shown in table 6 along with photochemical results for purposes of comparison.

TABLE 6

Comparison of radiochemical and photochemical temperature coefficients

TEMPERATURE INTERVAL	TEMPERATURE COEFFICIENTS				
	Radiochemical	Photochemical			
		Direct	Mercury sensitized		
			$P_{mm.\ Hg}$ 0.0004	$P_{mm.\ Hg}$ 0.0035	$P_{mm.\ Hg}$ 0.020
degrees C.					
183 to 25	1.00	—	—	—	—
100 to 200	1.039	1.045	—	—	—
200 to 300	1.043	1.07	—	—	—
300 to 400	1.047	1.07	1.12	1.09	1.05
400 to 500	1.047	—	—	—	—
400 to 490	—	1.13	1.08	1.07	1.05

DISCUSSION

The most outstanding feature of the temperature coefficient of this reaction is the complete absence of any influence of temperature from −185°C. to 25°C., a range of more than 200°C. On account of the lack of influence of temperature on the primary step, ionization, it might be supposed that any reaction resulting immediately and quantitatively from ionization should show no temperature coefficient. The fact that it does not in the lower temperature range furnishes evidence of two types of reaction, the stably quantized type, and at higher temperature, a chain mechanism of some kind.

For convenience one may assume for the low temperature range the ion "cluster" type such as has already been proposed for this and other reactions. At higher temperatures one would hardly expect the clusters to increase in size or efficiency of reaction, and it seems more probable to assume a breaking down of the cluster and a transition to some type of chain mechanism which ultimately leads to explosion. It is not improbable that the cluster mechanism persists and overlaps the chain mechanism, which gradually becomes predominant toward higher temperatures.

The complete efficiency of ions of water vapor in promoting the reaction is interesting, especially in view of the low efficiency (14 per cent) found by Rosenblum (9) of carbon dioxide ions in promoting the oxidation of carbon monoxide. In other cases however, there was ample analogy to support 100 per cent efficiency of foreign gas ions, also in this reaction (loc. cit.).

SUMMARY

The combination of hydrogen and oxygen under alpha radiation was studied at temperatures varying from −185°C. to +500°C., with radon mixed with the reacting gases and with radon in an alpha-ray bulb, with and without circulation of the gases.

The results obtained for the reaction at 25°C. agree with those previously obtained, viz., three molecules of water formed per ion pair (calculations being based on higher values of intensity of ionization than formerly). The reaction is found to proceed with approximately this same ion pair yield at −185°C. and at −78°C.

A positive temperature effect sets in above room temperature. The temperature coefficient is found to vary between 1.02 and 1.05. These values are compared with those found for the photochemical reaction.

The method of applying the correction for reaction due to ionic catalyst (water vapor) present in the system is considered. It is found that the ions of water vapor possess the same efficiency in producing reaction as the ions of the reacting gases themselves.

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THE THERMODYNAMICS OF THE ELECTROCAPILLARY CURVE. II

The Variation of the Electrocapillary Curve with Composition

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I. INTRODUCTION

In the preceding paper on this subject,[1] the following general equation was deduced for the electrocapillary curve (I, p. 126):

$$d\sigma = -s^{w}dT - \sum_{i=1}^{p^{\alpha}} \Gamma_i^{\alpha} d\mu_i^{\alpha} - \sum_{i=1}^{p^{\beta}} \Gamma_i^{\beta} d\mu_i^{\beta} - \sum_{k=1}^{r} \Gamma_k d\mu_k - \epsilon^{a} d[(\varphi^{\alpha} - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^{\beta}) - \mathfrak{T}] \tag{40}$$

It is the purpose of the present paper to deduce from this equation the special equations describing the variation of the electrocapillary curve with composition. The results are of value because they show how electrocapillary measurements are to be interpreted thermodynamically so as to yield the maximum amount of information about the composition of the electric double layer.

The system to which equation 40 applies is made up of three parts as follows: (1) two phases α and β constituting a perfectly polarizable system (I, p. 112 ff.); (2) a piece of some metal Me and a series of contiguous phases connecting it with α (I, p. 126); (3) another piece of the same metal Me and a series of contiguous phases connecting it with β. In general the composition of each of the parts 1, 2, and 3 is to be regarded as independently variable.

As regards the two phases α and β of the perfectly polarizable system proper, it will be recalled that they may have no charged components X_i in common (I, p. 116), i.e., that

$$p = p^{\alpha} + p^{\beta} \tag{1}$$

[1] This Journal **38**, 111 (1934); this paper will henceforth be referred to as I, the present paper as II. The equations in I and II are numbered as a single series: I contains equations 1 to 43 inclusive; II equations 44 to 168 inclusive. The reader is referred to I for the meaning of all mathematical symbols except those used for the first time in II.

Furthermore, in practice one of the two phases is always metallic, the other nonmetallic. Therefore the electrically neutral components X_k, being insoluble in metals under ordinary conditions, are in practice always confined to the nonmetallic phase, i.e., if, as is the case throughout this paper, α denote the metallic, β the nonmetallic phase, then (I, p. 117) $r^\alpha = 0$ and

$$r = r^\beta \tag{5}$$

Thus in practice the two phases never have any components, charged or neutral, in common, and therefore the composition of each phase interior may be varied independently of the other. Restricting equation 40 in accordance with equation 5 yields

$$\begin{aligned} d\sigma = &- s^w dT - \sum_{i=1}^{p^\alpha} \Gamma_i^\alpha d\mu_i^\alpha - \sum_{i=1}^{p^\beta} \Gamma_i^\beta d\mu_i^\beta - \sum_{k=1}^{r^\beta} \Gamma_k^\beta d\mu_k^\beta \\ &- \epsilon^\alpha d[(\varphi^\alpha - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^\beta) - \mathfrak{E}] \end{aligned} \tag{40.1}$$

This paper will be confined to the consequences of equation 40.1.

Throughout this paper it is assumed that the metallic phase α and the arbitrary metal Me are in *direct* contact without intervening phases. Besides the variation of α and β it is therefore necessary to consider only the variation in the above-mentioned part of the system. This part of the system shall henceforth be designated as the reference electrode (cf. I, p. 111). For example, if the system under consideration is

$$\overset{\mathrm{I}}{\mathrm{Me}} \mid \overset{\alpha}{\mathrm{Hg}} \mid \overset{\beta}{1\ N\ \mathrm{KNO_3}\ \text{solution}} \mid 1\ N\ \mathrm{HCl}\ \text{solution} \mid \mathrm{AgCl} \mid \mathrm{Ag} \mid \overset{\mathrm{II}}{\mathrm{Me}}$$

then the reference electrode is

$$\mathrm{Me} \mid \mathrm{Ag} \mid \mathrm{AgCl} \mid 1\ N\ \mathrm{HCl}\ \text{solution}$$

The problem is thus reduced to that of the independent variations of α, of β, and of the reference electrode. The effects of these three kinds of variation on the behavior of the system are accordingly considered separately below.

It is to be noted in advance that the equations derived below are perfectly exact only for the case in which the pressures P^α and P^β of α and β, respectively, are each constant, and that in order to apply these equations to the electrocapillary curves determined in the Lippmann electrometer, in which P^α varies slightly, it is necessary to assume that the quantities μ_i^α (equation 40.1) are independent of P^α within the limits defined by the inequality 42 (I, p. 127). The fact that equation 43 (I, p. 127), which rests upon this assumption, is experimentally verified, may be regarded as direct proof that there is no appreciable error connected with the assumption.

II. VARIATION OF THE ELECTROCAPILLARY CURVE WITH THE COMPOSITION OF THE REFERENCE ELECTRODE

Let the surface tension σ, the temperature T, the pressures P^α, P^β, and the composition of the phases α and β be kept constant, and let the reference electrode be varied as regards both the number and the composition of all its phases. Then equation 40.1 reduces to

$$d[(\varphi^\alpha - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^\beta) - \mathfrak{E}] = 0 \tag{44}$$

whence

$$(\varphi^\alpha - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^\beta) - \mathfrak{E} = \text{constant}^2 \tag{45}$$

$$\mathfrak{E} = -\text{ constant} + (\varphi^\alpha - \varphi^{\mathrm{I}}) + (\varphi^{\mathrm{II}} - \varphi^\beta) \tag{46}$$

Now consider two different reference electrodes which may be represented by

$$\mathrm{Me}_1 \underset{1}{|||} \quad \text{and} \quad \mathrm{Me}_2 \underset{2}{|||}$$

where the three vertical lines with the subscripts 1 and 2 indicate the presence of an arbitrary number of different phases in each case. For these two reference electrodes equation 46 may be written as

$$\mathfrak{E}_1 = -\text{ constant} + (\varphi^\alpha - \varphi^{\mathrm{I}})_1 + (\varphi^{\mathrm{II}} - \varphi^\beta)_1 \tag{47.1}$$

$$\mathfrak{E}_2 = -\text{ constant} + (\varphi^\alpha - \varphi^{\mathrm{I}})_2 + (\varphi^{\mathrm{II}} - \varphi^\beta)_2 \tag{47.2}$$

Subtraction of equation 47.2 from equation 47.1 gives

$$\mathfrak{E}_1 - \mathfrak{E}_2 = (\varphi^{\mathrm{I}} - \varphi^\alpha)_2 + (\varphi^\alpha - \varphi^{\mathrm{I}})_1 + (\varphi^{\mathrm{II}} - \varphi^\beta)_1 + (\varphi^\beta - \varphi^{\mathrm{II}})_2 \tag{48}$$

The quantity on the right side of equation 48 is evidently the E.M.F. of the combination

$$\mathrm{Me}_2 \mid \alpha \mid \mathrm{Me}_1 \underset{1}{|||} \beta \underset{2}{|||} \mathrm{Me}_2$$

which, since α is metallic, has the same E.M.F. as the cell formed out of the two reference electrodes by joining them through β. Changing from one reference electrode to another therefore displaces the electrocapillary curve of a given perfectly polarizable system horizontally by an amount equal to the E.M.F. of the cell formed by joining the two reference electrodes through β.

III. VARIATION OF THE ELECTROCAPILLARY CURVE WITH THE COMPOSITION OF THE METALLIC PHASE

Let the temperature T, the pressures P^α, P^β, the composition of the nonmetallic phase β and the composition of the reference electrode be

[2] Comparison of equation 45 with equation 39 (I, p. 126) shows that constant = $(\varphi^\alpha - \varphi^\beta)$.

regarded as constant, and only the composition of the metallic phase α and the applied potential $\mathfrak{E}$ be varied. Under these conditions the terms in T, μ_i^β, μ_k^β and $(\varphi^{\mathrm{II}} - \varphi^\beta)$ vanish from equation 40.1 leaving

$$d\sigma = -\sum_{i=1}^{p^\alpha} \Gamma_i^\alpha d\mu_i^\alpha - \epsilon^\alpha d(\varphi^\alpha - \varphi^{\mathrm{I}}) + \epsilon^\alpha d\mathfrak{E} \tag{49}$$

A. The case $p^\alpha = 2$

This case, the simplest possible, is trivial for the purpose in hand, because the interior of α can consist only of a single metal and is therefore incapable of variations of composition. The terms in μ_i^α and $(\varphi^\alpha - \varphi^{\mathrm{I}})$ accordingly drop out of equation 49, leaving the Lippmann-Helmholtz equation 41.

B. The general case of any number of charged components p^α

In this case the interior of α consists of a solution of a number q^α of metals such that (I, p. 116)

$$q^\alpha = p^\alpha - 1 \tag{2.1}$$

For this general case equation 49 is reducible to a simple form, first, because α being metallic all its charged components are of the same sign (positive) except one, namely the electron, and second, because α and Me being in *direct* contact, it is always the electron with respect to which α and Me are in electrochemical equilibrium.

Let μ_{j+}^α and $\mu_\ominus^\alpha$ be the chemical potentials (per equivalent) of the cations of the jth metal and of the electrons, respectively, in the interior of α and let Γ_{j+}^α, $\Gamma_\ominus^\alpha$ be the corresponding surface densities (in equivalents per unit area). The sum in equation 49 may then be written as

$$\sum_{i=1}^{p^\alpha} \Gamma_i^\alpha d\mu_i^\alpha = \sum_{j=1}^{q^\alpha} \Gamma_{j+}^\alpha d\mu_{j+}^\alpha + \Gamma_\ominus^\alpha d\mu_\ominus^\alpha \tag{50}$$

The introduction of the necessary relation

$$\mu_{j+}^\alpha = \mu_j^\alpha - \mu_\ominus^\alpha \tag{51}$$

where μ_j^α is the chemical potential per equivalent of the jth metal, into equation 50 gives

$$\sum_{i=1}^{p^\alpha} \Gamma_i^\alpha d\mu_i^\alpha = \sum_{j=1}^{q^\alpha} \Gamma_{j+}^\alpha d\mu_j^\alpha - \left(\sum_{j=1}^{q^\alpha} \Gamma_{j+}^\alpha - \Gamma_\ominus^\alpha\right) d\mu_\ominus^\alpha \tag{52}$$

From equation 33.1 it is evident that

$$\sum_{j=1}^{q^\alpha} \Gamma_{j+}^\alpha - \Gamma_\ominus^\alpha = \frac{\epsilon^\alpha}{F} \tag{53}$$

The substitution of equation 53 into equation 52 and of the result into equation 49 gives

$$d\sigma = -\sum_{j=1}^{q^\alpha} \Gamma_{j+}^{\alpha} d\mu_j^{\alpha} + \epsilon^\alpha d\frac{\mu_\Theta^\alpha}{F} - \epsilon^\alpha d(\varphi^\alpha - \varphi^{\mathrm{I}}) + \epsilon^\alpha d\mathfrak{E} \tag{54}$$

Now since α and Me are in electrochemical equilibrium as regards the electron,

$$\varphi^\alpha - \varphi^{\mathrm{I}} = \frac{\mu_\Theta^\alpha - \mu_\Theta^{\mathrm{I}}}{F} \tag{55}$$

where μ_Θ^{I} is the chemical potential of the electron in Me. But since the composition of the reference electrode and therefore that of Me is constant, μ_Θ^{I} is constant and hence

$$d(\varphi^\alpha - \varphi^{\mathrm{I}}) = d\frac{\mu_\Theta^\alpha}{F} \tag{56}$$

so that equation 54 becomes

$$d\sigma = -\sum_{j=1}^{q^\alpha} \Gamma_{j+}^{\alpha} d\mu_j^{\alpha} + \epsilon^\alpha d\mathfrak{E} \tag{57}$$

The μ_j^α in this equation are of course subject to the Gibbs-Duhem relation at constant T and P^α, which may be written as

$$\sum_{j=1}^{q^\alpha} N_j^\alpha d\mu_j^\alpha = 0 \tag{58}$$

where N_j^α is the equivalent fraction of the jth metal, defined in analogy to the mole fraction by

$$N_j^\alpha = \frac{n_j^\alpha}{\sum_{j'=1}^{q^\alpha} n_{j'}^\alpha} \tag{59}$$

n_j^α and $n_{j'}^\alpha$ being the number of *equivalents* of the jth and the j'^{th} metal in a given mass of the interior of the phase α. The simultaneous equations 57 and 58 give a complete thermodynamic account of the case of any number of metals at constant temperature and pressure.

C. The case $p^\alpha = 3$

In this case the interior of α consists of a solution of two metals. Let the subscript 1 refer to the solvent metal; subscript 2 to the solute metal. Then equations 57 and 58 become, respectively,

$$d\sigma = -\Gamma^{\alpha}_{1+}d\mu^{\alpha}_{1+} - \Gamma^{\alpha}_{2+}d\mu^{\alpha}_{2+} + \epsilon^{\alpha}d\mathfrak{E} \tag{60}$$

$$N^{\alpha}_{1}d\mu^{\alpha}_{1} + N^{\alpha}_{2}d\mu^{\alpha}_{2} = 0 \tag{61}$$

The elimination of the chemical potential of the solvent metal, μ^{α}_{1}, from equations 60 and 61 gives

$$d\sigma = \left(\frac{N^{\alpha}_{2}}{N^{\alpha}_{1}}\Gamma^{\alpha}_{1+} - \Gamma^{\alpha}_{2+}\right)d\mu^{\alpha}_{2} + \epsilon^{\alpha}d\mathfrak{E} \tag{62}$$

This equation yields for the vertical shift of the electrocapillary maximum with μ^{α}_{2} (by setting $\epsilon^{\alpha} = 0$ according to equation 41)

$$\frac{\partial\sigma^{\max}}{\partial\mu^{\alpha}_{2}} = \frac{N^{\alpha}_{2}}{N^{\alpha}_{1}}\Gamma^{\alpha\,\max}_{1+} - \Gamma^{\alpha\,\max}_{2+} \tag{63}$$

for the vertical shift of the electrocapillary curve

$$\left(\frac{\partial\sigma}{\partial\mu^{\alpha}_{2}}\right)_{\mathfrak{E}} = \frac{N^{\alpha}_{2}}{N^{\alpha}_{1}}\Gamma^{\alpha}_{1+} - \Gamma^{\alpha}_{2+} \tag{64}$$

for the horizontal shift of the electrocapillary curve

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^{\alpha}_{2}}\right)_{\sigma} = -\frac{1}{\epsilon^{\alpha}}\left(\frac{N^{\alpha}_{2}}{N^{\alpha}_{1}}\Gamma^{\alpha}_{1+} - \Gamma^{\alpha}_{2+}\right) \tag{65}$$

For sufficiently small values of N^{α}_{2} the terms in $\frac{N^{\alpha}_{2}}{N^{\alpha}_{1}}\Gamma^{\alpha}_{1+}$ in equations 63, 64, and 65 may be neglected; this yields the approximate relations

$$\frac{\partial\sigma^{\max}}{\partial\mu^{\alpha}_{2}} = -\Gamma^{\alpha\,\max}_{2+} \tag{66}$$

$$\left(\frac{\partial\sigma}{\partial\mu^{\alpha}_{2}}\right)_{\mathfrak{E}} = -\Gamma^{\alpha}_{2+} \tag{67}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^{\alpha}_{2}}\right)_{\sigma} = \frac{\Gamma^{\alpha}_{2+}}{\epsilon^{\alpha}} \tag{68}$$

so that from the shift of the curve with composition, the adsorption of the solute metal ions in a sufficiently dilute metallic solution may be calculated if the thermodynamic properties of the solution are known. It is to be noted that the equations lead to no relation giving Γ^{α}_{1+} or Γ^{α}_{θ} in terms of experimentally observable quantities, so that the knowledge of the composition of the metallic side of the double layer obtainable from thermodynamics alone, while valuable, is incomplete. Equation 67 is essentially identical with an equation given by Frumkin (2).

IV. VARIATION OF THE ELECTROCAPILLARY CURVE WITH THE COMPOSITION OF THE NONMETALLIC PHASE

Let the temperature T, the pressures P^α, P^β the composition of the metallic phase α, and the composition of the reference electrode be kept constant, and only the composition of the nonmetallic phase β and the applied potential $\mathfrak{E}$ be varied. Under these conditions the terms in T, μ_i^α, and $(\varphi^\alpha - \varphi^{\mathrm{I}})$ vanish from equation 40.1, leaving

$$d\sigma = -\sum_{i=1}^{p^\beta} \Gamma_i^\beta d\mu_i^\beta - \sum_{k=1}^{r^\beta} \Gamma_k^\beta d\mu_k^\beta - \epsilon^\alpha d(\varphi^{\mathrm{II}} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \tag{69}$$

Owing to the possibility of more than one kind of charged component of each sign in β as well as of neutral components, and furthermore of various types of electrochemical behavior at the junction between β and the reference electrode, this case is more complicated than that of the metallic phase α. As a result equation 69, in contrast to equation 49, is not reducible to a simpler form without added restrictions. The discussion is therefore profitably limited to a number of special cases of physical interest.

A. The case $p^\beta = 2$

This case, the simplest possible, is trivial because the interior of β can consist only of a single electrolyte[3] dissociating into two kinds of ions (e.g., a molten salt), so that variations of composition are impossible. Equation 69 reduces to the Lippmann-Helmholtz equation (41).

B. The case $p^\beta = 2$, $r^\beta = 1$

In this case the interior of β contains one electrolyte dissociating into two kinds of ions and one nonelectrolyte. The best examples are electrolyte solutions in certain organic solvents, e.g., lithium chloride in acetone. Aqueous electrolyte solutions come under this case only in so far as the dissociation of the water may be neglected; as shown later (II, p. 361) this is possible without serious error in certain special cases. In the following treatment the nonelectrolyte is regarded as the solvent in the interior of β, the electrolyte as the solute, because this is the situation met with in practice.

Let μ_+^β and μ_-^β be the chemical potentials (per equivalent) of the cation and anion of the electrolyte, and μ_0^β the chemical potential (per mole) of

[3] In the present discussion of the nonmetallic phase, the term "electrolyte" will be used in its special, and usual, sense, and not in the general sense of "electrolyte component," as defined in I, p. 115.

the nonelectrolyte. Let Γ_+^β, Γ_-^β, and Γ_0^β be the corresponding surface densities. Equation 69 then becomes

$$d\sigma = -\Gamma_+^\beta d\mu_+^\beta - \Gamma_-^\beta d\mu_-^\beta - \Gamma_0^\beta d\mu_0^\beta - \epsilon^\alpha d(\varphi^{II} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \tag{70}$$

The substitution of

$$\mu_+^\beta = \mu^\beta - \mu_-^\beta \tag{71.1}$$

or alternatively of

$$\mu_-^\beta = \mu^\beta - \mu_+^\beta \tag{71.2}$$

where μ^β is the chemical potential per equivalent of electrolyte, yields

$$d\sigma = -\Gamma_0^\beta d\mu_0^\beta - \Gamma_\pm^\beta d\mu^\beta \pm (\Gamma_+^\beta - \Gamma_-^\beta)\, d\mu_\mp^\beta - \epsilon^\alpha d(\varphi^{II} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \tag{72}$$

where the two alternative equations are written as a single equation with double signs. Since by equations 33.2 and 10.2

$$\Gamma_+^\beta - \Gamma_-^\beta = \frac{\epsilon^\beta}{F} \tag{73.1}$$

$$= -\frac{\epsilon^\alpha}{F} \tag{73.2}$$

equation 72 becomes

$$d\sigma = -\Gamma_0^\beta d\mu_0^\beta - \Gamma_\pm^\beta d\mu^\beta \mp \epsilon^\alpha d\frac{\mu_\mp^\beta}{F} - \epsilon^\alpha d(\varphi^{II} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \tag{74}$$

The chemical potentials μ_0^β and μ^β are subject to the Gibbs-Duhem relation

$$N_0^\beta d\mu_0^\beta + N^\beta d\mu^\beta = 0 \tag{75}$$

in which N_0^β, N^β are defined similarly to mole fractions by

$$N_0^\beta = \frac{n_0^\beta}{n_0^\beta + n^\beta} \qquad N^\beta = \frac{n^\beta}{n_0^\beta + n^\beta} \tag{76.1) (76.2}$$

where n_0^β and n^β are the number of moles of nonelectrolyte and equivalents of electrolyte, respectively, in a given mass of the interior of β. Since the nonelectrolyte is regarded as the solvent, it is expedient to eliminate μ_0^β from equations 74 and 75; this gives

$$d\sigma = \left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_\pm^\beta\right) d\mu^\beta \mp \epsilon^\alpha d\frac{\mu_\mp^\beta}{F} - \epsilon^\alpha d(\varphi^{II} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \tag{77}$$

For the vertical shift of the electrocapillary maximum ($\epsilon^\alpha = 0$) with μ^β, equation 77 yields

$$\frac{\partial\sigma^{max}}{\partial\mu^\beta} = \frac{N^\beta}{N_0^\beta}\Gamma_0^{\beta max} - \Gamma_\pm^{\beta max} \tag{78}$$

The double sign remaining in this equation can be eliminated, because on setting $\epsilon^\alpha = 0$ in equation 73.2 it appears that

$$\Gamma_+^{\beta\max} = \Gamma_-^{\beta\max} \tag{79}$$

so that it is permissible to set

$$\Gamma_\pm^{\beta\max} = \Gamma_{\text{electrolyte}}^{\beta\max} \tag{80}$$

and equation 78 becomes

$$\frac{\partial\sigma^{\max}}{\partial\mu^\beta} = \frac{N^\beta}{N_0^\beta}\Gamma_0^{\beta\max} - \Gamma_{\text{electrolyte}}^{\beta\max} \tag{81}$$

In sufficiently dilute solutions of the electrolyte the term $\frac{N^\beta}{N_0^\beta}\Gamma_0^{\beta\max}$ is negligible and equation 81 becomes

$$\frac{\partial\sigma^{\max}}{\partial\mu^\beta} = -\Gamma_{\text{electrolyte}}^{\beta\max} \tag{82}$$

This equation may be taken as the basis for the distinction between capillary-inactive $\left(\frac{\partial\sigma^{\max}}{\partial\mu^\beta} \sim 0\right)$ and capillary-active $\left(\frac{\partial\sigma^{\max}}{\partial\mu^\beta} < 0\right)$ electrolytes in a given nonelectrolyte solvent.

The further consequences of the alternative equations 77 depend upon the electrochemical behavior of the junction between the phase β (of variable composition) and the reference electrode (of constant composition). The following two cases are of physical interest:

Special case 1. The potential difference $(\varphi^{\text{II}} - \varphi^\beta)$ is given either by the equation

$$\varphi^{\text{II}} - \varphi^\beta = \text{constant} + \frac{\mu_+^\beta}{F} \tag{83.1}$$

or by the equation

$$\varphi^{\text{II}} - \varphi^\beta = \text{constant} - \frac{\mu_-^\beta}{F} \tag{83.2}$$

If $(\varphi^{\text{II}} - \varphi^\beta)$ is given by equation 83.1, then the reference electrode will be said to *respond simply to the cation* of β. Example:

$$\overset{\text{I}}{\text{Me}} \mid \overset{\alpha}{\text{Hg}} \mid \text{KNO}_3 \text{ solution of } \overset{\beta}{\text{variable concentration}} \mid \text{K amalgam of constant concentration} \mid \overset{\text{II}}{\text{Me}}$$

And if $(\varphi^{\text{II}} - \varphi^\beta)$ is given by equation 83.2, the reference electrode will be said to *respond simply to the anion* of β. Example:

$$\overset{\text{I}}{\text{Me}} \mid \overset{\alpha}{\text{Hg}} \mid \text{KCl solution of } \overset{\beta}{\text{variable concentration}} \mid \text{HgCl} \mid \text{Hg} \mid \overset{\text{II}}{\text{Me}}$$

Special case 2. The junction between β and the reference electrode is a "liquid–liquid junction." Example:

$$\overset{\mathrm{I}}{\mathrm{Me}} \mid \overset{\alpha}{\mathrm{Hg}} \mid \overset{\beta}{\mathrm{KNO_3\ solution\ of\ variable\ concentration}} \mid \overset{\gamma}{1N\ \mathrm{H_2SO_4}} \mid \mathrm{Hg_2SO_4} \mid \mathrm{Hg} \mid \overset{\mathrm{II}}{\mathrm{Me}}$$

in which the solvent[4] in the phases β and γ is the same.

Of these two special cases, the first is the simpler theoretically, but special case 2 is the only one which has hitherto been investigated experimentally.

Special case 1. The reference electrode responds simply either to the cation or the anion of β. If it responds simply to the cation it follows from equation 83.1 that

$$\mathrm{d}\,(\varphi^{\mathrm{II}} - \varphi^{\beta}) = \mathrm{d}\,\frac{\mu_+^{\beta}}{F} \tag{84.1}$$

and hence from equation 77 with the lower sign that

$$\mathrm{d}\sigma = \left(\frac{N^{\beta}}{N_0^{\beta}}\,\Gamma_0^{\beta} - \Gamma_-^{\beta}\right)\mathrm{d}\mu^{\beta} + \epsilon^{\alpha}\mathrm{d}\mathfrak{E} \tag{85.1}$$

If, on the other hand, the reference electrode responds simply to the anion of β, it follows from equation 83.2 that

$$\mathrm{d}\,(\varphi^{\mathrm{II}} - \varphi^{\beta}) = -\,\mathrm{d}\,\frac{\mu_-^{\beta}}{F} \tag{84.2}$$

and hence from equation 77 with the upper sign that

$$\mathrm{d}\sigma = \left(\frac{N^{\beta}}{N_0^{\beta}}\,\Gamma_0^{\beta} - \Gamma_+^{\beta}\right)\mathrm{d}\mu^{\beta} + \epsilon^{\alpha}\mathrm{d}\mathfrak{E} \tag{85.2}$$

Equations 85.1 and 85.2 yield the following relations for the shift of the electrocapillary curve with μ^{β}: if the reference electrode responds simply to the

cation of β	*anion of β*	
$\left(\frac{\partial\sigma}{\partial\mu^{\beta}}\right)_{\mathfrak{E}} = \frac{N^{\beta}}{N_0^{\beta}}\,\Gamma_0^{\beta} - \Gamma_-^{\beta}$	$\left(\frac{\partial\sigma}{\partial\mu^{\beta}}\right)_{\mathfrak{E}} = \frac{N^{\beta}}{N_0^{\beta}}\,\Gamma_0^{\beta} - \Gamma_+^{\beta}$	(86.1) (86.2)
$\left(\frac{\partial\mathfrak{E}}{\partial\mu^{\beta}}\right)_{\sigma} = -\frac{1}{\epsilon^{\alpha}}\left(\frac{N^{\beta}}{N_0^{\beta}}\,\Gamma_0^{\beta} - \Gamma_-^{\beta}\right)$	$\left(\frac{\partial\mathfrak{E}}{\partial\mu^{\beta}}\right)_{\sigma} = -\frac{1}{\epsilon^{\alpha}}\left(\frac{N^{\beta}}{N_0^{\beta}}\,\Gamma_0^{\beta} - \Gamma_+^{\beta}\right)$	(87.1) (87.2)

[4] In so far as the solutions used in the examples for the above cases 1 and 2 are considered to be aqueous, the electrolyte dissociation of the water is neglected here. As shown in II, p. 361, this assumption leads to no serious error in a number of cases.

For sufficiently small values of N^β equations 86.1 to 87.2 lead to the approximate relations

$$\left(\frac{\partial\sigma}{\partial\mu^\beta}\right)_{\mathfrak{E}} = -\Gamma^\beta_- \qquad \left(\frac{\partial\sigma}{\partial\mu^\beta}\right)_{\mathfrak{E}} = -\Gamma^\beta_+ \qquad (88.1)\ (88.2)$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^\beta}\right)_\sigma = \frac{\Gamma^\beta_-}{\epsilon^\alpha} \qquad \left(\frac{\partial\mathfrak{E}}{\partial\mu^\beta}\right)_\sigma = \frac{\Gamma^\beta_+}{\epsilon^\alpha} \qquad (89.1)\ (89.2)$$

so that from the shift of the curve with composition, the adsorption of the solute cation or anion in a sufficiently dilute solution may be calculated, if the thermodynamic properties of the solution are known. Any one of the equations 88.1 to 89.2 together with equations 73.1 and 73.2 and the Lippmann-Helmholtz equation (41) evidently leads to a complete knowledge of the ionic content of the nonmetallic side of the double layer in this case.

Special case 2. The junction between β and the reference electrode is a liquid–liquid junction. This case may be represented schematically as follows:

$$\overset{\mathrm{I}}{\mathrm{Me}} \mid \alpha \mid \beta \mid \gamma \mid\mid\mid \overset{\mathrm{II}}{\mathrm{Me}}$$

in which $\mathrm{Me} \mid\mid\mid \gamma$ is the reference electrode, and the liquid–liquid junction $\beta \mid \gamma$ is made up in some definite and reproducible manner. The system thus represented will be referred to as system S. In order to apply equation 77 it is expedient to consider besides system S also the following cell, henceforth designated as system S′:

$$\overset{\mathrm{III}}{\mathrm{Me}} \underset{1}{\mid\mid\mid} \beta \mid \gamma \mid\mid\mid \overset{\mathrm{IV}}{\mathrm{Me}}$$

In this cell the electrode $\mathrm{Me} \mid\mid\mid \gamma$ and the liquid–liquid junction $\beta \mid \gamma$ are supposed to be identical with the reference electrode and the junction $\beta \mid \gamma$, respectively, in system S. The electrode $\mathrm{Me} \underset{1}{\mid\mid\mid}$ of system S′ is supposed to be any electrode whatever which responds simply to either the cation or the anion of β as defined under special case 1 (II, p. 347), and will henceforth be referred to as electrode 1. The Roman numerals I, II, III, IV serve merely to label, for the purposes of discussion, the four separate pieces of the *same* metal Me which form the terminals of S and S′.

The quantity $(\varphi^{\mathrm{II}} - \varphi^\beta)$ occurring in equation 77 may now be transformed as follows:

$$\varphi^{\mathrm{II}} - \varphi^\beta = (\varphi^{\mathrm{II}} - \varphi^\beta)_{\mathrm{S}} = (\varphi^{\mathrm{IV}} - \varphi^\beta)_{\mathrm{S}'} \qquad (90)$$

$$= (\varphi^{\mathrm{III}} - \varphi^\beta)_{\mathrm{S}'} + (\varphi^{\mathrm{IV}} - \varphi^{\mathrm{III}})_{\mathrm{S}'} \qquad (91)$$

$$= (\varphi^{\mathrm{III}} - \varphi^\beta)_{\mathrm{S}'} + \mathfrak{E}' \qquad (92)$$

where the subscripts S and S′ indicate the systems to which the corresponding quantities in parenthesis refer, and $\mathfrak{E}'$ is the E.M.F. of the cell, system S′, defined by

$$\mathfrak{E}' = (\varphi^{\mathrm{IV}} - \varphi^{\mathrm{III}})_{S'} \tag{93}$$

The introduction of equation 92 into equation 77 gives

$$d\sigma = \left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_\pm^\beta\right) d\mu^\beta \mp \epsilon^\alpha d\frac{\mu_\mp^\beta}{F} - \epsilon^\alpha d(\varphi^{\mathrm{III}} - \varphi^\beta)_{S'} - \epsilon^\alpha d\mathfrak{E}' \mp \epsilon^\alpha d\mathfrak{E} \tag{94}$$

If now electrode 1 responds simply to the cation of β it follows in analogy to equation 84.1 that

$$d(\varphi^{\mathrm{III}} - \varphi^\beta)_{S'} = d\frac{\mu_+^\beta}{F} \tag{95.1}$$

and hence from equation 94 with the lower sign that

$$d\sigma = \left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_-^\beta\right) d\mu^\beta - \epsilon^\alpha d\mathfrak{E}' + \epsilon^\alpha d\mathfrak{E} \tag{96.1}$$

Similarly if electrode 1 responds simply to the anion of β it follows in analogy to equation 84.2 that

$$d(\varphi^{\mathrm{III}} - \varphi^\beta)_{S'} = -d\frac{\mu_-^\beta}{F} \tag{95.2}$$

and hence from equation 94 with the upper sign that

$$d\sigma = \left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_+^\beta\right) d\mu^\beta - \epsilon^\alpha d\mathfrak{E}' + \epsilon^\alpha d\mathfrak{E} \tag{96.2}$$

Equations 96.1 and 96.2 yield the following relations for the shift of the electrocapillary curve with μ^β : if electrode 1 responds simply to the

cation of β

$$\left(\frac{\partial\sigma}{\partial\mu^\beta}\right)_{\mathfrak{E}} = \frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_-^\beta - \epsilon^\alpha\frac{\partial\mathfrak{E}'}{\partial\mu^\beta} \tag{97.1}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^\beta}\right)_\sigma = -\frac{1}{\epsilon^\alpha}\left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_-^\beta\right) + \frac{\partial\mathfrak{E}'}{\partial\mu^\beta} \tag{98.1}$$

anion of β

$$\left(\frac{\partial\sigma}{\partial\mu^\beta}\right)_{\mathfrak{E}} = \frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_+^\beta - \epsilon^\alpha\frac{\partial\mathfrak{E}'}{\partial\mu^\beta} \tag{97.2}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu^\beta}\right)_\sigma = -\frac{1}{\epsilon^\alpha}\left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_t^\beta\right) + \frac{\partial\mathfrak{E}'}{\partial\mu^\beta} \tag{98.2}$$

In sufficiently dilute solutions the terms in $\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta$ may be neglected as in special case 1.

The comparison of equations 97.1 to 98.2 with equations 86.1 to 87.2 shows that special case 2 leads to exactly the same information regarding the double layer as special case 1, provided $\frac{\partial \mathfrak{E}'}{\partial \mu^\beta}$ is known. In general, the only way of obtaining accurate values of $\frac{\partial \mathfrak{E}'}{\partial \mu^\beta}$ is by experiment, because the cell S′ contains a liquid–liquid junction (variable with β) and the exact thermodynamic equations for the E.M.F. of such cells contain so many unknown factors as to be useless practically. The situation may be illustrated by considering a particular system, for instance, the system given as an example of special case 2 in II, p. 348. A possible choice for the corresponding system S′ is the following:

$$\overset{\text{III}}{\text{Me}} \,|\, \text{K amalgam of constant concentration} \,|\, \overset{\beta}{\text{KNO}_3 \text{ solution of variable concentration}} -$$

$$\overset{\gamma}{1\ N\ \text{H}_2\text{SO}_4} \,|\, \text{Hg}_2\text{SO}_4 \,|\, \text{Hg} \,|\, \overset{\text{IV}}{\text{Me}}$$

The exact equations for the E. M. F. $\mathfrak{E}'$ of this cell are:[5]

$$\mathfrak{E}' = \mathfrak{E}_{\text{El}} + \mathfrak{E}_{\text{D}} + \mathfrak{E}_{\text{S}} \tag{99}$$

where

$$\mathfrak{E}_{\text{El}} = \mathfrak{E}_0 - \frac{RT}{F}\ln c^\beta_{\text{K}^+} - \frac{RT}{2F}\ln c^\gamma_{\text{SO}_4^=} \tag{100}$$

$$\mathfrak{E}_{\text{D}} = \frac{RT}{F}\left\{\int_\gamma^\beta t_{\text{K}^+}\text{d}\ln c_{\text{K}^+} + \int_\gamma^\beta t_{\text{H}^+}\text{d}\ln c_{\text{H}^+} - \int_\gamma^\beta t_{\text{NO}_3^-}\text{d}\ln c_{\text{NO}_3^-} - \tfrac{1}{2}\int^\beta t_{\text{SO}_4^=}\text{d}\ln c_{\text{SO}_4^=}\right\} \tag{101}$$

$$\mathfrak{E}_{\text{s}} = \frac{3RT}{2F}\left\{\int_\gamma^\beta t_{\text{K}^+}\text{d}\ln f_{\text{K}^+,\,\text{SO}_4^=} + \int^\beta t_{\text{H}^+}\text{d}\ln f_{\text{H}^+,\,\text{SO}_4^=} + \int_\gamma^\beta t_{\text{NO}_3^-}\text{d}\ln\left[(f_{\text{K}^+,\,\text{NO}_3^-})^{-\frac{1}{3}}\cdot f_{\text{K}^+,\,\text{SO}_4^=}\right] - \ln f^\beta_{\text{K}^+,\,\text{SO}_4^=}\right\} \tag{102}$$

$\mathfrak{E}_{\text{El}}$ is the ideal value of that part of the total E.M.F. which is due to the two electrode potentials of the cell S′, $\mathfrak{E}_{\text{D}}$ is the ideal value of the diffusion

[5] The exact thermodynamic treatment of cells with liquid–liquid junctions is due to P. B. Taylor (5) and E. A. Guggenheim (3). Equations 99 to 102 were derived by the methods of these authors, so that the inclusion of the derivation here is unnecessary.

potential at the liquid–liquid junction between β and γ, and $\mathfrak{E}_S$ takes account of the deviations of the two electrode potentials and of the diffusion potential from their ideal values; c and t denote the concentration in equivalents per liter of solution and the transference number in equivalents per faraday, respectively, of the ion indicated in the subscript; f denotes the mean activity coefficient of the salt corresponding to the ions indicated in the subscript; $\mathfrak{E}^0$ is a constant. The evaluation of the integrals in equations 101 and 102 necessitates a knowledge of the values of c, t, and f both in the interiors of β and γ and at every point of the intermediate diffusion layer, and is therefore at present impossible. It follows that the calculation of accurate values of $\frac{\partial \mathfrak{E}'}{\partial \mu^\beta}$ from such equations as 99 to 102 is also impossible at the present state of knowledge. As a rule, therefore, the complete thermodynamic interpretation of the electrocapillary data in special case 2 necessitates supplementary measurements of the E. M. F. of cells of the type S′.

In at least one case of physical interest, however, the theoretical expression for $\frac{\partial \mathfrak{E}'}{\partial \mu^\beta}$ is simple enough to be of practical value. This case is defined by the following two conditions: (1) The phase γ of the reference electrode contains only one electrolyte which is the same as that in β. (2) The reference electrode responds simply to either the cation or the anion of γ, i.e., if the concentration of the electrolyte in γ were varied, then

$$(\varphi^{\mathrm{II}} - \varphi^\gamma)_s = (\varphi^{\mathrm{IV}} - \varphi^\gamma)_{s'} = \begin{cases} \text{either:} \quad \text{constant} + \dfrac{\mu_+^\gamma}{F} & (103.1) \\[2ex] \text{or:} \quad \text{constant} - \dfrac{\mu_-^\gamma}{F} & (103.2) \end{cases}$$

The simplicity of this case arises from the circumstance that electrode 1 of system S′ may always be chosen so that the ion of β to which it responds simply is the same as the ion of γ to which the reference electrode responds simply; for such cells S′ it is readily shown[6] that

$$d\mathfrak{E}' = -\frac{t_+^\beta}{F}\, d\mu^\beta \text{ if the two electrodes respond simply to the cation} \qquad (104.1)$$

$$d\mathfrak{E}' = \frac{t_-^\beta}{F}\, d\mu^\beta \text{ if the two electrodes respond simply to the anion} \qquad (104.2)$$

An example of a system S fulfilling the above conditions is

I	α	β	γ	II
Me	Hg	KCl solution of variable concentration	1 N KCl | HgCl	Hg | Me

[6] By the methods used in deriving equations 99 to 102. See II, footnote 5; also reference 4.

The corresponding system S′ is

III				β	γ			IV
Me	Hg	HgCl	KCl solution of variable concentration		1 N KCl	HgCl	Hg	Me

which obeys equation 104.2. The introduction of equations 104.1 and 104.2 respectively into equations 96.1 and 96.2 yields the equations

$$d\sigma = \left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_-^\beta + \frac{\epsilon^\alpha t_-^\beta}{F}\right) d\mu^\beta + \epsilon^\alpha d\mathfrak{T} \tag{105.1}$$

$$d\sigma = \left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_+^\beta - \frac{\epsilon^\alpha t_+^\beta}{F}\right) d\mu^\beta + \epsilon^\alpha d\mathfrak{T} \tag{105.2}$$

which give for the shift of the electrocapillary curve, if the reference electrode responds simply to the

cation of γ

$$\left(\frac{\partial\sigma}{\partial\mu^\beta}\right)_{\mathfrak{T}} = \frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_-^\beta + \frac{\epsilon^\alpha t_-^\beta}{F} \tag{106.1}$$

$$\left(\frac{\partial\mathfrak{T}}{\partial\mu^\beta}\right)_\sigma = -\frac{1}{\epsilon^\alpha}\left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_-^\beta\right) - \frac{t_-^\beta}{F} \tag{107.1}$$

anion of γ

$$\left(\frac{\partial\sigma}{\partial\mu^\beta}\right)_{\mathfrak{T}} = \frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_+^\beta - \frac{\epsilon^\alpha t_+^\beta}{F} \tag{106.2}$$

$$\left(\frac{\partial\mathfrak{T}}{\partial\mu^\beta}\right)_\sigma = -\frac{1}{\epsilon^\alpha}\left(\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta - \Gamma_+^\beta\right) + \frac{t_+^\beta}{F} \tag{107.2}$$

In sufficiently dilute solutions the terms in $\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta$ may be neglected as before.

Finally a semiquantitative general result useful in dilute solutions is obtainable by the following approximations: (1) The deviation of the solution in β from ideality is neglected. (2) The liquid–liquid junction between β and γ is neglected. (3) The term $\frac{N^\beta}{N_0^\beta}\Gamma_0^\beta$ is neglected. From approximation 1 it follows that

$$d\mu_+^\beta = \frac{RT}{z_+^\beta}\, d\ln c^\beta \tag{108.1}$$

$$d\mu_-^\beta = -\frac{RT}{z_-^\beta}\, d\ln c^\beta \tag{108.2}$$

$$d\mu^\beta = \frac{z_-^\beta - z_+^\beta}{z_-^\beta\, z_+^\beta}\, RT\, d\ln c^\beta \tag{109}$$

where z_+^β, z_-^β are the valences (with sign included) of the cation and anion in β and c^β is the equivalent concentration of the electrolyte. Furthermore from equation 93 it follows that

$$d\mathfrak{E}' = d(\varphi^{IV} - \varphi^{III})_{s'} \tag{110}$$

$$= -d(\varphi^{III} - \varphi^{\beta})_{s'} + d(\varphi^{IV} - \varphi^{\beta})_{s'} \tag{111}$$

which on introduction of equation 95.1 or 95.2 becomes

$$d\mathfrak{E}' = -d\frac{\mu_+^\beta}{F} + d(\varphi^{IV} - \varphi^{\beta})_{s'} \text{ if electrode 1 responds simply to the cation of } \beta \tag{112.1}$$

$$d\mathfrak{E}' = d\frac{\mu_-^\beta}{F} + d(\varphi^{IV} - \varphi^{\beta})_{s'} \text{ if electrode 1 responds simply to the anion of } \beta \tag{112.2}$$

By approximation 2 the term $d(\varphi^{IV} - \varphi^{\beta})_{s'}$ drops out; the substitution of equations 108.1 and 108.2 respectively into equations 112.1 and 112.2 then gives

$$d\mathfrak{E}' = -\frac{RT}{z_+^\beta F} d\ln c^\beta \tag{113.1}$$

$$d\mathfrak{E}' = -\frac{RT}{z_-^\beta F} d\ln c^\beta \tag{113.2}$$

Introducing equation 113.1 into equation 96.1, equation 113.2 into equation 96.2, and furthermore equation 109 and approximation 3 into both equation 96.1 and 96.2 yields the *alternative* equations

$$d\sigma = RT\left[\frac{z_+^\beta - z_-^\beta}{z_+^\beta z_-^\beta}\Gamma_\pm^\beta + \frac{\epsilon^\alpha}{z_\mp^\beta F}\right] d\ln c^\beta + \epsilon^\alpha d\mathfrak{E} \tag{114}$$

That these equations (114) are alternative is proved by the fact that one of them is obtainable from the other by the substitution of

$$\Gamma_\pm^\beta = \Gamma_\mp^\beta \mp \frac{\epsilon^\alpha}{F} \tag{115}$$

obtained from equation 73.2.

Equation 114 gives for the shift of the electrocapillary curve with concentration

$$\frac{\partial\sigma^{max}}{\partial\ln c^\beta} = RT\frac{z_+^\beta - z_-^\beta}{z_+^\beta z_-^\beta}\Gamma^{\beta}_{\text{electrolyte}}{}^{max} \tag{116}$$

$$\left(\frac{\partial\sigma}{\partial\ln c^\beta}\right)_{\mathfrak{E}} = RT\left[\frac{z_+^\beta - z_-^\beta}{z_+^\beta z_-^\beta}\Gamma_\pm^\beta + \frac{\epsilon^\alpha}{z_\mp^\beta F}\right] \tag{117}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\ln c^\beta}\right)_{\sigma} = RT\left[\frac{z_-^\beta - z_+^\beta}{z_+^\beta z_-^\beta}\cdot\frac{\Gamma_\pm^\beta}{\epsilon^\alpha} - \frac{1}{z_\mp^\beta F}\right] \tag{118}$$

For the special case of a capillary-inactive electrolyte at points along the electrocapillary curve sufficiently far removed from the maximum equation 118 may be integrated with the aid of a further approximation. In such an electrolyte the adsorption Γ_+^β, Γ_-^β of the two ions is due wholly to the electrostatic attraction of the charged metal surface, specific chemical forces being absent. Along the ascending branch $\epsilon^\alpha > 0$, so that the metal surface attracts anions and repels cations, whence $\Gamma_-^\beta > 0$, $\Gamma_+^\beta < 0$. At points far removed from the maximum, where ϵ^α is relatively large, Γ_+^β, because it is negative and the solution is dilute, is still relatively small numerically, so that for the lower part of the ascending branch the ratio $\frac{\Gamma_+^\beta}{\epsilon^\alpha}$ becomes negligible in equation 118. Setting $\frac{\Gamma_+^\beta}{\epsilon^\alpha} = 0$ in equation 118 (upper sign) gives

$$\left(\frac{\partial \mathfrak{E}}{\partial \ln c^\beta}\right)_\sigma = -\frac{RT}{z_-^\beta F} \tag{119.1}$$

which may be integrated at constant σ, giving for the horizontal displacement of the ascending branch with concentration,

$$\mathfrak{E}_2 - \mathfrak{E}_1 = -\frac{RT}{z_-^\beta F} \ln \frac{c_2^\beta}{c_1^\beta} \tag{120.1}$$

Similarly for the lower part of the descending branch $\frac{\Gamma_-^\beta}{\epsilon^\alpha}$ may be neglected and equation 118 (lower sign) gives

$$\left(\frac{\partial \mathfrak{E}}{\partial \ln c^\beta}\right)_\sigma = -\frac{RT}{z_+^\beta F} \tag{119.2}$$

$$\mathfrak{E}_2 - \mathfrak{E}_1 = -\frac{RT}{z^\beta F} \ln \frac{c_2^\beta}{c_1^\beta} \tag{120.2}$$

Equations 120.1 and 120.2 have already been given by Frumkin (1, 2).

C. The case $p^\alpha = 3$

In this case the interior of β consists of two electrolytes of two ions each, one of these ions being common to both electrolytes. The common ion may be either a cation or an anion. The best examples are aqueous solutions of acids (cation H^+ in common) and of metallic hydroxides (anion OH^- in common).

Special case 1. The common ion is a cation. In this case equation 69 becomes

$$d\sigma = -\Gamma_+^\beta d\mu_+^\beta - \Gamma_{1-}^\beta d\mu_{1-}^\beta - \Gamma_{2-}^\beta d\mu_{2-}^\beta - \epsilon^\alpha d(\varphi^{II} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \tag{121}$$

in which the subscript + refers to the cation, and the subscripts 1− and 2− to the anions of the solvent and the solute respectively. The substitution into equation 121 of the two relations

$$\mu_{1-}^{\beta} = \mu_1^{\beta} - \mu_+^{\beta} \tag{122.1}$$

$$\mu_{2-}^{\beta} = \mu_2^{\beta} - \mu_+^{\beta} \tag{122.2}$$

where μ_1 and μ_2 are the chemical potentials per equivalent of solvent and solute respectively, yields

$$d\sigma = -\Gamma_{1-}^{\beta}\, d\mu_1^{\beta} - \Gamma_{2-}^{\beta}\, d\mu_2^{\beta} - (\Gamma_+^{\beta} - \Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta})\, d\mu_+^{\beta} - \epsilon^{\alpha} d(\varphi^{\mathrm{II}} - \varphi^{\beta}) + \epsilon^{\alpha} d\mathfrak{E} \tag{123}$$

From equations 33.2 and 10.2 it follows that

$$\Gamma_+^{\beta} - \Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta} = \frac{\epsilon^{\beta}}{F} \tag{124.1}$$

$$= -\frac{\epsilon^{\alpha}}{F} \tag{124.2}$$

and hence from equation 123 that

$$d\sigma = -\Gamma_{1-}^{\beta} d\mu_1^{\beta} - \Gamma_2^{\beta} - d\mu_{2-}^{\beta} + \epsilon^{\alpha} d\frac{\mu_+^{\beta}}{F} - \epsilon^{\alpha} d(\varphi^{\mathrm{II}} - \varphi^{\beta}) + \epsilon^{\alpha} d\mathfrak{E} \tag{125}$$

which, on elimination of μ_1^{β} by means of the Gibbs-Duhem relation:

$$N_1^{\beta} d\mu_2^{\beta} + N_2^{\beta} d\mu_2^{\beta} = 0 \tag{126}$$

gives

$$d\sigma = \left(\frac{N_2^{\beta}}{N_1^{\beta}}\Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta}\right) d\mu_2^{\beta} + \epsilon^{\alpha} d\frac{\mu_+^{\beta}}{F} - \epsilon^{\alpha} d(\varphi^{\mathrm{II}} - \varphi^{\beta}) + \epsilon^{\alpha} d\mathfrak{E} \tag{127}$$

where N_1^{β} and N_2^{β} are the equivalent fractions (cf. equation 59) of solvent and solute respectively.

For the shift of $\sigma^{\max}$ with μ_2^{β} equation 127 yields

$$\frac{\partial\sigma^{\max}}{\partial\mu_2^{\beta}} = \frac{N_2^{\beta}}{N_1^{\beta}}\Gamma_{1-}^{\beta\max} - \Gamma_{2-}^{\beta\max} \tag{128}$$

in which the term $\frac{N_2^{\beta}}{N_1^{\beta}}\Gamma_{1-}^{\beta\max}$ is negligible in sufficiently dilute solutions, giving the approximate relation

$$\frac{\partial\sigma^{\max}}{\partial\mu_2^{\beta}} = -\Gamma_{2-}^{\beta\max} \tag{129}$$

The further consequences of equation 127 depend upon the nature of the junction between β and the reference electrode. The following four special cases 1α, 1β, 1γ, 1δ are of physical interest.

Special case 1α. The reference electrode responds simply to the cation of β, i.e.,

$$d(\varphi^{II} - \varphi^{\beta}) = d\,\frac{\mu_+^{\beta}}{F} \tag{130}$$

The introduction of equation 130 into equation 127 gives

$$d\sigma = \left(\frac{N_2^{\beta}}{N_1^{\beta}}\Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta}\right) d\mu_2^{\beta} + \epsilon^{\alpha} d\mathfrak{E} \tag{131}$$

This equation yields for the shift of the electrocapillary curve with μ_2^{β}

$$\left(\frac{\partial\sigma}{\partial\mu_2^{\beta}}\right)_{\mathfrak{E}} = \frac{N_2^{\beta}}{N_1^{\beta}}\Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta} \tag{132}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu_2^{\beta}}\right)_{\sigma} = -\frac{1}{\epsilon^{\alpha}}\left(\frac{N_2^{\beta}}{N_1^{\beta}}\Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta}\right) \tag{133}$$

in which the term $\frac{N_2^{\beta}}{N_1^{\beta}}\Gamma_{1-}^{\beta}$ may be neglected in sufficiently dilute solutions giving the approximate relations

$$\left(\frac{\partial\sigma}{\partial\mu_2^{\beta}}\right)_{\mathfrak{E}} = -\Gamma_{2-}^{\beta} \tag{134}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu_2^{\beta}}\right)_{\sigma} = \frac{\Gamma_{2-}^{\beta}}{\epsilon^{\alpha}} \tag{135}$$

Special case 1β. The reference electrode responds simply to the anion of the solvent in β, i.e.,

$$d(\varphi^{II} - \varphi^{\beta}) = -\,d\,\frac{\mu_{1-}^{\beta}}{F} \tag{136}$$

The substitution of the relation

$$\mu_+^{\beta} = \mu_1^{\beta} - \mu_{1-}^{\beta} \tag{137}$$

into equation 127, and of equations 136 and 126 into the result yields

$$d\sigma = \left[\frac{N_2^{\beta}}{N_1^{\beta}}\left(\Gamma_{1-}^{\beta} - \frac{\epsilon^{\alpha}}{F}\right) - \Gamma_{2-}^{\beta}\right] d\mu_2^{\beta} + \epsilon^{\alpha} d\mathfrak{E} \tag{138}$$

This equation gives for the shift of the electrocapillary curve with μ_2^{β}

$$\left(\frac{\partial\sigma}{\partial\mu_2^{\beta}}\right)_{\mathfrak{E}} = \frac{N_2^{\beta}}{N_1^{\beta}}\left(\Gamma_{1-}^{\beta} - \frac{\epsilon^{\alpha}}{F}\right) - \Gamma_{2-}^{\beta} \tag{139}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu_2^{\beta}}\right)_{\sigma} = -\frac{1}{\epsilon^{\alpha}}\left[\frac{N_2^{\beta}}{N_1^{\beta}}\left(\Gamma_{1-}^{\beta} - \frac{\epsilon^{\alpha}}{F}\right) - \Gamma_{2-}^{\beta}\right] \tag{140}$$

in which the term $\frac{N_2^{\beta}}{N_1^{\beta}}\left(\Gamma_{1-}^{\beta} - \frac{\epsilon^{\alpha}}{F}\right)$ may be neglected in sufficiently dilute solution giving again equations 134 and 135.

Special case 1γ. The reference electrode responds simply to the anion of the solute, i.e.,

$$d(\varphi^{II} - \varphi^{\beta}) = - d \frac{\mu_{2-}^{\beta}}{F} \tag{141}$$

The substitution of the relation

$$\mu_{+}^{\beta} = \mu_{2}^{\beta} - \mu_{2-}^{\beta} \tag{142}$$

into equation 127, and of equation 141 into the result yields

$$d\sigma = \left(\frac{N_2^{\beta}}{N_1^{\beta}} \Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta} + \frac{\epsilon^{\alpha}}{F}\right) d\mu_2^{\beta} + \epsilon^{\alpha} d\mathfrak{E} \tag{143}$$

This equation gives for the shift of the electrocapillary curve with μ_2^{β}

$$\left(\frac{\partial\sigma}{\partial\mu_2^{\beta}}\right)_{\mathfrak{E}} = \frac{N_2^{\beta}}{N_1^{\beta}} \Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta} + \frac{\epsilon^{\alpha}}{F} \tag{144}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu_2^{\beta}}\right)_{\sigma} = - \frac{1}{\epsilon^{\alpha}} \left(\frac{N_2^{\beta}}{N_1^{\beta}} \Gamma_{1-}^{\beta} - \Gamma_{2-}^{\beta}\right) - \frac{1}{F} \tag{145}$$

in which the term $\frac{N_2^{\beta}}{N_1^{\beta}} \Gamma_{1-}^{\beta}$ may be neglected in sufficiently dilute solutions giving the approximate relations

$$\left(\frac{\partial\sigma}{\partial\mu_2^{\beta}}\right)_{\mathfrak{E}} = - \Gamma_{2-}^{\beta} + \frac{\epsilon^{\alpha}}{F} \tag{146}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu_2^{\beta}}\right)_{\sigma} = \frac{\Gamma_{2-}^{\beta}}{\epsilon^{\alpha}} - \frac{1}{F} \tag{147}$$

From equations 129, 134, 146, and 41, it is evident that from the shift of the electrocapillary curve with composition, the adsorption of the solute anion in a sufficiently dilute solution may be calculated in the cases considered, if the thermodynamic properties of the solution are known. It is to be noted that the equations lead to no relation giving Γ_{+}^{β} or Γ_{1-}^{β} in terms of experimentally observable quantities, so that the information obtainable, while valuable is incomplete. The situation regarding the nonmetallic side of the double layer for $p^{\beta} = 3$ is therefore similar to that regarding the metallic side in the case $p^{\alpha} = 3$ (II, p. 344; cf. particularly equations 128, 129, 131, 132, 133, 134 and 135 with equations 63, 66, 62, 64, 65, 67, 68).

Special case 1δ. The junction between β and the reference electrode is a liquid–liquid junction. By means of supplementary E.M.F. measurements

of suitable cells this special case can always be reduced to one of the foregoing special cases 1α, 1β, 1γ, in exactly the same way as for $p^\beta = 2$, $r^\beta = 1$, special case 2 is reducible to special case 1 by means of the cells S′ (II, pp. 349–355).

Special case 2 (of the case $p^\beta = 3$). The common ion is an anion. The results for this special case are immediately obtainable from those for special case 1 by replacing the word "cation" in the discussion of special case 1 by "anion" and vice versa, and, in equations 121, 128, 129, 131 to 135, 138 to 140, 143 to 147, replacing the + in the subscripts by − and vice versa.

D. The case $p^\beta = 4$

This case is so complicated that a general treatment is inexpedient. There is only one special case simple enough to be worth considering here.

Special case 1. This case is defined by two conditions: (1) The interior of β consists of two electrolytes of two ions each, there being no common ion. (2) The ions of the solvent electrolyte are not specifically adsorbed. This special case is of importance because it includes the aqueous solutions of certain neutral salts.

Under condition 1 equation 69 becomes

$$d\sigma = -\Gamma^\beta_{1+}d\mu^\beta_{1+} - \Gamma^\beta_{-1}d\mu^\beta_{2-} - \Gamma^\beta_{2+}d\mu^\beta_{2+} - \Gamma^\beta_{2-}d\mu^\beta_{2-} - \epsilon^\alpha d(\varphi^{II} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{T} \quad (148)$$

where the subscripts 1+, 1− refer to cation and anion of the solvent electrolyte, 2+, 2− to cation and anion of the solute electrolyte. Condition 2 means that

$$\Gamma^\beta_{1+} = \Gamma^\beta_{1-} \quad (149)$$

so that it is permissible to set

$$\Gamma^\beta_{1\pm} = \Gamma^\beta_1 \quad (150)$$

where Γ^β_1 is the surface density of the solvent molecules (in equivalents per unit area). The substitution of equation 150 and of the relation

$$\mu^\beta_{1+} + \mu^\beta_{1-} = \mu^\beta_1 \quad (151)$$

into equation 148 gives

$$d\sigma = -\Gamma^\beta_1 d\mu^\beta_1 - \Gamma^\beta_{2+}d\mu^\beta_{2+} - \Gamma^\beta_{2-}d\mu^\beta_{2-} - \epsilon^\alpha d(\varphi^{II} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{T} \quad (152)$$

If the subscripts 1, 2+, 2− are replaced by 0, +, −, respectively, equation 152 becomes identical with equation 70 for the case $p^\beta = 2$, $r^\beta = 1$ (II, pp. 345–355). Moreover, under condition 1 above the interior of β contains only two independently variable components, so that the Gibbs-Duhem equation for the case in hand is similar to equation 75 for the case $p^\beta = 2$, $r^\beta = 1$ in that it contains only two terms, namely

$$N^\beta_1 d\mu^\beta_1 + N^\beta_2 d\mu^\beta_2 = 0 \quad (153)$$

where μ_1^β is given by equation 151 and μ_2 by

$$\mu_{2+}^\beta + \mu_{2-}^\beta = \mu_2^\beta \tag{154}$$

and N_1^β, N_2^β are the equivalent fractions of solvent and solute. It follows that all the consequences of equations 152 and 153 are identical in form with those of equations 70 and 75, i.e., under the above conditions 1 and 2 the effect of the dissociation of the solvent electrolyte disappears and the case $p^\beta = 4$ reduces to the case $p^\beta = 2$, $r^\beta = 1$.

Frumkin (2) has shown how it is always possible to ascertain experimentally whether the above condition 2 is approximately fulfilled by an aqueous solution of a neutral salt. The method consists in investigating the shift in the electrocapillary curve of the salt solution produced by adding to the solution a small quantity of either that acid or that metallic hydroxide of which the salt in question is the product of neutralization. The junction between the salt solution (β) and the reference electrode must be a liquid–liquid junction. If no appreciable shift is found, equation 149 applies; if there is a shift, equation 149 does not apply. The theory of the method is best explained by means of a special case, say sodium sulfate solution. For this case equation 148 becomes

$$\begin{aligned} d\sigma = &- \Gamma_{H^+}^\beta d\mu_{H^+}^\beta - \Gamma_{OH^-}^\beta d\mu_{OH^-}^\beta - \Gamma_{Na^+}^\beta d\mu_{Na^+}^\beta - \Gamma_{SO_4^=}^\beta d\mu_{SO_4^=}^\beta \\ &- \epsilon^\alpha d(\varphi^{II} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \end{aligned} \tag{155}$$

The substitution of

$$\mu_{H^+}^\beta = \mu_{H_2O}^\beta - \mu_{OH^-}^\beta \tag{156}$$

gives

$$\begin{aligned} d\sigma = &(\Gamma_{H^+}^\beta - \Gamma_{OH^-}^\beta)\, d\mu_{OH^-}^\beta - \Gamma_{H^+}^\beta d\mu_{H_2O}^\beta - \Gamma_{Na^+}^\beta d\mu_{Na^+}^\beta - \Gamma_{SO_4^=}^\beta d\mu_{SO_4^=}^\beta \\ &- \epsilon^\alpha d(\varphi^{II} - \varphi^\beta) + \epsilon^\alpha d\mathfrak{E} \end{aligned} \tag{157}$$

Consider the change in σ at constant $\mathfrak{E}$ produced by adding to a sodium sulfate solution of constant concentration, say 1 N, an amount of sodium hydroxide, say 0.01 equivalent per liter, so small that the values of $\mu_{H_2O}^\beta$, $\mu_{Na^+}^\beta$, $\mu_{SO_4^=}^\beta$, $(\varphi^{II} - \varphi^\beta)$ are not appreciably affected, but yet large enough to change $\mu_{H^+}^\beta$ and $\mu_{OH^-}^\beta$ appreciably. For such a change equation 157 gives

$$\frac{\partial\sigma}{\partial\mu_{OH^-}^\beta} \sim \Gamma_{H^+}^\beta - \Gamma_{OH^-}^\beta \tag{158}$$

If no shift of the curve is observed, $\dfrac{\partial\sigma}{\partial\mu_{OH^-}^\beta} = 0$ and it follows that

$$\Gamma_{H^+}^\beta \sim \Gamma_{OH^-}^\beta \tag{159}$$

i.e., condition 2 is at least approximately fulfilled. But if an appreciable shift is observed then $\frac{\partial\sigma}{\partial\mu^{\beta}_{OH^-}} \neq 0$ and

$$\Gamma^{\beta}_{H^+} \neq \Gamma^{\beta}_{OH^-} \tag{160}$$

Similarly it can be shown that the absence of a shift on adding a small amount of sulfuric acid to the sodium sulfate solution is also a criterion for the approximate fulfillment of condition 2. Frumkin has found that 1 N sodium sulfate + 0.01 N sulfuric acid and 1 N sodium sulfate + 0.01 N sodium hydroxide both have electrocapillary curves practically identical with that of 1 N sodium sulfate, and that 1 N potassium thiocyanate + 0.01 N thiocyanic acid and 1 N potassium thiocyanate + 0.01 N potassium hydroxide both have electrocapillary curves practically identical with that of 1 N potassium thiocyanate (2). It follows that the equations for the case $p^{\beta} = 2$, $r^{\beta} = 1$ apply to these solutions.

Case E. The concentrations in the phase β are constant save for that of a dilute, powerfully adsorbed nonelectrolyte

A typical example of this case is the system

$$\overset{\alpha}{Hg} \mid 1\,N\,Na_2SO_4 + 0.02N\,H_2SO_4 + \text{tert.}\,\overset{\beta}{C_5H_{11}OH} \text{ in the concentration } c'^{\beta}$$

where $0 \leq c'^{\beta} \leq$ about 0.05 molal. The variation of c'^{β} throughout this relatively small range causes a relatively enormous variation of σ. Almost any organic nonelectrolyte in aqueous solution behaves similarly to the tertiary amyl alcohol. The equations of physical interest yielded by this case are all only approximate, but they have the advantage of applying no matter what the composition of β is. The approximation consists in neglecting the effect of variations in the concentration, c'^{β}, of the substance in question upon the chemical potentials μ^{β}_i, μ^{β}_k of the other components of β and upon the quantity $(\varphi^{II} - \varphi^{\beta})$. Equation 69 shows this approximation to be the better, the smaller the concentration and the greater the absorbability of the substance is. Introducing this approximation into equation 69 gives

$$d\sigma = -\Gamma'^{\beta}d\mu'^{\beta} + \epsilon^{\sigma}d\mathfrak{E} \tag{161}$$

where Γ'^{β} and μ'^{β} are respectively the surface density in moles per unit area and the chemical potential per mole of the component of variable concentration. This equation yields for the shift of the electrocapillary curve with μ'^{β} the approximate relations

$$\frac{\partial\sigma^{max}}{\partial\mu'^{\beta}} = -\Gamma'^{\beta}_{max} \tag{162}$$

$$\left(\frac{\partial\sigma}{\partial\mu'^{\beta}}\right)_{\mathfrak{E}} = -\Gamma'^{\beta} \tag{163}$$

$$\left(\frac{\partial\mathfrak{E}}{\partial\mu'^{\beta}}\right)_{\sigma} = \frac{\Gamma'^{\beta}}{\epsilon^{\alpha}} \tag{164}$$

The equations 162, 163, 164 yield immediately useful results on setting

$$d\mu'^{\beta} = RT\, d\ln c'^{\beta} \tag{165}$$

a good approximation for most nonelectrolytes in the concentration range in which equations 161 to 164 are reasonably accurate.

V. REMARK ON THE RELATION BETWEEN THE VERTICAL AND THE HORIZONTAL SHIFT OF THE ELECTROCAPILLARY CURVE WITH COMPOSITION

In five of the cases discussed above, namely III C ($p^{\alpha} = 3$), IV B ($p^{\beta} = 2$, $r^{\beta} = 1$), IV C ($p^{\beta} = 3$), IV D, special case 1 ($p^{\beta} = 4$, special case 1), IV E (concentrations in β constant save for that of dilute, powerfully adsorbable nonelectrolyte), the state of that phase whose composition is varied is a function of but a single variable, which may be designated by λ and taken to mean the chemical potential of one of the components of the phase in question, or its mole fraction, or its equivalent concentration, or any other variable of composition. Hence in the five cases mentioned the surface tension σ is a function of only two variables, which may be taken as the arbitrary variable of composition λ and the applied potential $\mathfrak{E}$. It follows from the rules of partial differentiation that

$$\left(\frac{\partial\sigma}{\partial\lambda}\right)_{\mathfrak{E}} = -\left(\frac{\partial\sigma}{\partial\mathfrak{E}}\right)_{\lambda}\cdot\left(\frac{\partial\mathfrak{E}}{\partial\lambda}\right)_{\sigma} \tag{166}$$

But since T, P^{α}, P^{β} are constant, equation 41 gives

$$\left(\frac{\partial\sigma}{\partial\mathfrak{E}}\right)_{\lambda} = \epsilon^{\alpha} \tag{167}$$

whence

$$\left(\frac{\partial\sigma}{\partial\lambda}\right)_{\mathfrak{E}} = -\epsilon^{\alpha}\cdot\left(\frac{\partial\mathfrak{E}}{\partial\lambda}\right)_{\sigma} \tag{168}$$

Equation 168 is the general and exact relation between the vertical and horizontal shift of the electrocapillary curve with composition in the five cases enumerated above. It is seen to be fulfilled by all the above pairs of equations, either exact or approximate, in which the vertical and horizontal shifts of the curve with some variable of composition are given separately, e.g. by the pairs 64 and 65, 67 and 68, 86 and 87, 97 and 98, 117 and 118, etc.

VI. SUMMARY

In the systems giving rise to electrocapillary curves the reference electrode, the metallic phase α and the nonmetallic phase β can each be varied in composition independently. The principal equations describing the effect of each of these three kinds of variation on the electrocapillary curve are deduced for the first time, starting from a general equation derived in a previous paper. As regards variations of the reference electrode and of the metallic phase α, the general equations describing their effect upon the electrocapillary curve (equations 48 and 57, 58, respectively) are relatively simple. But for variations of the nonmetallic phase β the possibilities are so diverse that no simple general expression can be obtained, and it is therefore necessary to consider the chief special cases separately. In many of the cases considered the surfaced ensities Γ_i, Γ_k of certain components of the electric double layer can be approximately calculated from the shift of the electrocapillary curve caused by varying the composition of α or of β.

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THE THERMAL DECOMPOSITION OF GASEOUS ETHYLENE IODIDE

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Ethylene iodide decomposes readily, even at moderate temperatures and in the absence of oxygen, into ethylene and iodine. This thermal decomposition has been studied recently by several investigators. Pollissar (5) used carbon tetrachloride as a solvent and found that iodine was a catalyst for the reaction, the rate being proportional to the product of the ethylene iodide concentration and the square root of the iodine concentration. He concluded that iodine atoms were the real catalytic agents, and he devised some equations to satisfy the kinetics of the reaction. Schumacher and Wiig (6) made a photochemical study of the influence of iodine atoms on the decomposition. In 1928 Mooney and Ludlam (4) published a paper dealing with the dissociation pressure of ethylene iodide, the gaseous equilibria of the gases ethylene iodide, iodine, and ethylene at different temperatures in the presence of solid ethylene iodide and iodine, and a few experiments on the velocity of decomposition of gaseous ethylene iodide, and of the substance dissolved in carbon tetrachloride, in which they concluded that iodine played the part of a catalyst. Mooney (4) recently carried out some experiments on the synthesis of ethylene iodide from ethylene and iodine, and found that the reaction took place on the surface of the solid iodine, and that the glass surface of the reaction vessel was not, in itself, catalytic unless covered with a layer of alcohol. A satisfactory investigation of the rate of decomposition of the purely gaseous substance does not seem to have been undertaken. This paper is a record of some experiments we have carried out under these conditions, and of our own conclusions, which differ in some respects from those of previous workers.

We found, at the outset, that ethylene iodide which was in the slightest degree impure was quite useless for quantitative work. We prepared the pure substance by passing ethylene into an alcoholic solution of iodine containing powdered glass, which was a very efficient catalyst, though not all varieties of glass were found suitable for this purpose. The substance was recrystallized several times from alcohol, was of a pure white appearance, and melted sharply at 82°C.

The reaction was carried out in a glass vessel (figure 1) and the change in

pressure recorded on a simple glass manometer. It will be seen from the figure that one side of this could be opened continuously to the vacuum system if necessary. The manometric liquid was a very concentrated solution (at 65°C.) of orthophosphoric acid, obtained by partially dehydrating the ordinary commercial phosphoric acid. It was heated under the vacuum until dissolved gases were removed. After opening T_1 (figure 1) to the vacuum system, and closing T_2 for a time, no perceptible pressure difference was detected.

We carried out some preliminary tests and found that neither iodine vapor nor ethylene were appreciably soluble in this liquid. It was the only one of a number we experimented with which satisfactorily fulfilled

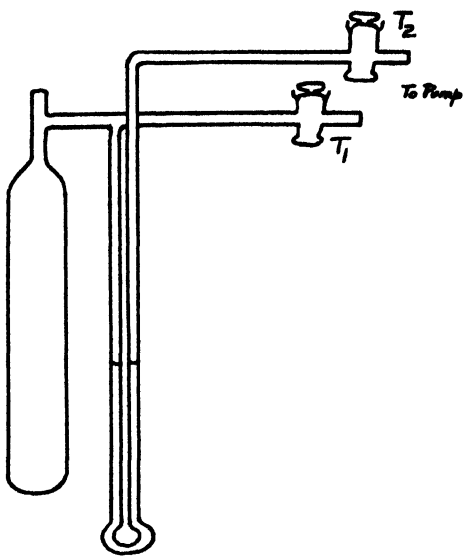

FIG. 1. GLASS REACTION VESSEL

these conditions. The manometer was read from outside the thermostat, in which both it and the reaction vessel were immersed, by means of a cathetometer.

The reaction vessel was cleaned in the usual way with chromic acid, etc., but in some cases we used hydrofluoric acid. These modes of treating the glass surface have a marked influence on the reaction rate. No attempt was made to bake out the vessel at a temperature much higher than that of the reaction itself.

The taps T_1 and T_2 were lubricated with graphite and metaphosphoric acid, and in some experiments we discarded T_1 and sealed off directly.

The decomposition was studied at 65°C. and 75°C. The procedure was this: A small quantity of ethylene iodide was introduced through the top

of the reaction vessel, which was then sealed up and evacuated with a Hyvac pump. The solid ethylene iodide remained at the bottom of the vessel and was prevented from vaporizing completely by cooling with a freezing mixture of ice and salt. The final pressure under these condi-

TABLE 1

The decomposition of ethylene iodide at 65°C.

Experiment no. 9. Induction period pronounced

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$	$k_2 \times 10^6$	$k_2(\sqrt{I_2}) \times 10^5$	$k_2(I_2) \times 10^5$
minutes	*mm.* H_3PO_4					
10	19.6					
15	19.9					
25	20.4					
30	20.7					
40	20.7					
50	20.7					
60	22 4	170	372			
70	23.2	125	280		33	90
80	24 0	110	252		30	79
90	24.5	95			27	64
100	25.6	98	255		30	65
110	26 5	97	238		31	61
120	27.8	101	261		36	61
130	28.6	99	261		37	51
140	29 6	101	271		40	56
150	30 8	102	291		46	55
160	31 9	101	307		51	54
170	32 8	100	318		56	52
180	33 7	99	330		62	51
190	34.5	97	341		69	50
200	35.3	94	354		77	49
210	35 7	92	350	869	80	46
220	36.3	89	358	914		46
230	36.7	85	358	919		44
240	36.9	80	349	1007		43
250	37.4	78	357	1023		42
260	37 6		351	1009		41
270	37.7		339	998		39
280	37 8		330	945		37
310	38 0					
320	38.0					

tions was not much more than the limit obtained by the pump, namely, 0.001 mm. of mercury. We tried solid carbon dioxide as a cooling agent, but found that ethylene iodide was too unstable at this low temperature; some decomposition took place as was apparent from the brown color developed by the ethylene iodide on the side adjacent to the cold glass

surface. It may be that the excessive refrigeration condenses some very volatile substance which acts as a catalyst for the decomposition, or there is another crystalline form of ethylene iodide which is unstable. Unless the ethylene iodide used is very pure, the reaction will not exhibit the special features now to be described.

The reaction vessel was plunged into the thermostat at 65°C. and immediate readings of the manometer taken. As the ethylene iodide va-

TABLE 2

The decomposition of ethylene iodide at 65°C.

Experiment no. 13. Induction period pronounced

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$	$k_2(I_2) \times 10^6$	$k_2 \times 10^6$
minutes	*mm.* H_3PO_4				
10	(9.3)				
15	9.1				
20	9.2				
25	9.2				
30	9.2				
35	9.2				
45	9.8	(60)			
60	10.1	36		174	
75	10.8	40	208	145	
90	11.2	36	194	130	
105	11.8	36	198	122	
120	12 2	35	202	109	
135	12.5	33	193	96	
165	13.3	32	197	92	
180	13.7	31	201	88	
195	14.1	31	206	84	
210	14.4	30	207	79	808
225	14.6	28	202	65	813
285	15.2	24	194	56	797
330	15.4	21	165	53	762
360	15.7	20		45	805
390	15.9	19			820
405	15 9				
420	15.9				

porized and acquired the temperature of the thermostat, the pressure rose and remained steady for a while. No trace of iodine vapor could be detected in the vessel. The pressure began to increase again, and plotting the pressure against the time, we obtained the type of curve shown in figure 2 (curve A). Towards the end of the reaction a definite violet vapor filled the reaction vessel. If the ethylene iodide used was partially decomposed or if a small crystal of iodine was introduced into the reaction vessel before sealing up, the form of the curve was different (figure 2,

curve B). The pressure never remained steady at any time. Undoubtedly the portion ab of the curve A indicates an induction period, and it seemed reasonable, at first, to attribute this to the lack of the necessary catalytic agent, presumably iodine, which, however, soon begins to accumulate in the system, with consequent increase in the speed of decomposition. We would expect the reaction to be bimolecular and to follow an equation of the second order, involving either the iodine concentration or its square root. But this does not seem to be the case. The results of a number of our experiments have been tabulated. We calculated the velocity con-

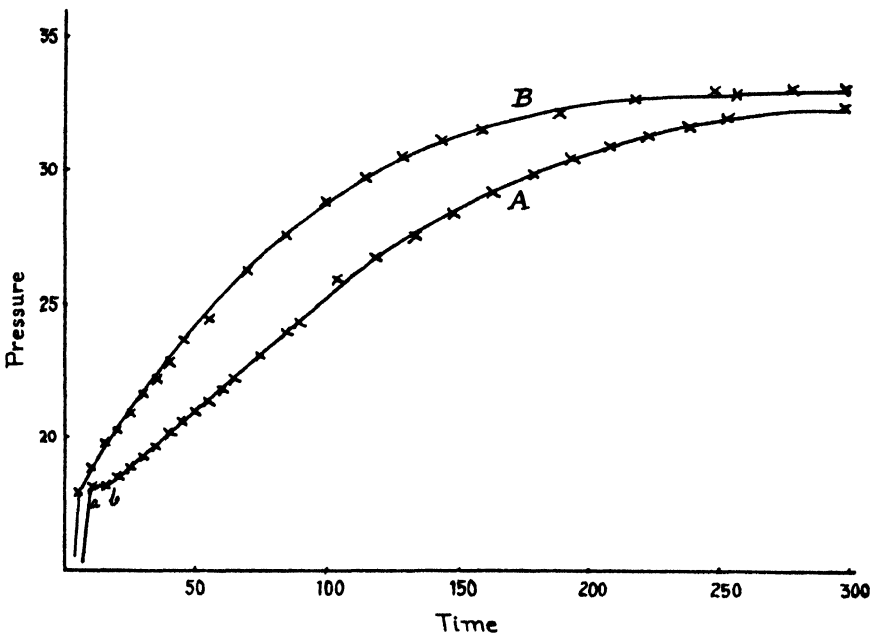

FIG. 2. DECOMPOSITION OF ETHYLENE IODIDE AT 65°C.

Curve A, experiment no. 14; curve B, experiment no. 15

stants k_0, k_1, k_2 (I_2), k_2 ($\sqrt{I_2}$) and k_2, for the zero order, monomolecular, bimolecular (catalyzed), and bimolecular (uncatalyzed), respectively.

If a = initial concentration of ethylene iodide (in millimeters of phosphoric acid), x = concentration of iodine formed, and t = time in minutes, then

$$\frac{dx}{dt} = -\frac{d(a-x)}{dt} = K \qquad (K = K_0, \text{ zero order}) \qquad (1)$$

$$\frac{dx}{dt} = K(a-x),\ K = \frac{1}{t}\ln\frac{a}{a-x} \qquad (K = K_1, \text{ monomolecular}) \qquad (2)$$

$$\frac{dx}{dt} = K(a - x)x,\ K(t_2 - t_1) = \frac{1}{a}\left(\ln \frac{x_2\,(a - x_1)}{x_1\,(a - x_2)}\right)$$

$$(K = K_2\ (I_2)\ \text{bimolecular catalyzed}) \qquad (3)$$

$$\frac{dx}{dt} = K(a - x)\sqrt{x},\ K(t_2 - t_1) = \frac{1}{\sqrt{a}}\left(\ln \frac{(\sqrt{a} + \sqrt{x_2})\,(\sqrt{a} - \sqrt{x_1})}{(\sqrt{a} - \sqrt{x_2})\,(\sqrt{a} + \sqrt{x_1})}\right)$$

$$(K = K_2\ (\sqrt{I_2})\ \text{bimolecular catalyzed}) \qquad (4)$$

$$\frac{dx}{dt} = K(a - x)^2,\ K = \frac{1}{t}\,\frac{x}{a(a - x)} \qquad (K = K_2,\ \text{bimolecular uncatalyzed}) \qquad (5)$$

The initial pressure was taken to be the pressure recorded during the induction period.

The rate of decomposition is best represented by the zero order equation in the first stage, and after the pressure has fallen, by the monomolecular equation, and finally by the bimolecular equation (uncatalyzed). This is characteristic of a heterogeneous reaction, where strong adsorption takes place on the walls of the vessel.

We verified the heterogeneous nature of the reaction by introducing a number of thin glass tubes into the reaction vessel. There is an increase in the velocity of decomposition, and the reaction follows the same course as before. A similar increase in the velocity is obtained by cleaning the reaction vessel with a dilute solution of hydrofluoric acid. There must be an increase in the number of active centers of adsorption as the result of this procedure, but this does not explain the induction period.

We could assume that iodine is a catalyst for the decomposition. If the reaction were mainly homogeneous it would be of the second order, as Pollissar found in carbon tetrachloride. There is undoubtedly a slow homogeneous reaction at 65°C., but the heterogeneous reaction is the more rapid, and we can only conclude that there is some reaction between the ethylene iodide and the iodine on the glass walls of the reaction vessel.

Iodine is not so strongly adsorbed on glass as on calcium fluoride, according to de Boer (1). But these effects are relative, and iodine is found to be adsorbed more readily on freshly blown glass surfaces, or on glass that has been treated with hydrofluoric acid. We find that in the vacuum system from which mercury vapor has not been removed by liquid air, and into which iodine vapor is admitted, deposits of mercuric iodide are found mostly on the internal surfaces of the glass joints that have been heated by the hand blowpipe. This is a suggestive but by no means conclusive demonstration of the selective nature of iodine adsorption on glass.

In all the experiments we observed that the reaction did not appear to go to completion; there seemed to be some undecomposed ethylene iodide remaining, as the pressure was not sufficiently great for complete decom-

position. Mooney and Ludlam (4) found an equilibrium constant at 65°C. which indicated almost complete decomposition, and for this reason we felt justified in using the simple kinetic equations. We also came to the same conclusion in some preliminary experiments at 65°C., in which ethylene and iodine vapor were mixed; there was no perceptible pressure

TABLE 3

The decomposition of ethylene iodide at 75°C.

Experiment no. 14. Short induction period

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$	$k_2 \times 10^5$	$k_2(\sqrt{I_2}) \times 10^5$	$k_2(I_2) \times 10^5$
minutes	*mm.* H_3PO_4					
10	18.1					
15	18 1					
20	18.5	80	194		171	344
25	18 9	80	197		209	252
30	19.2	73	182		215	222
35	19.6	75	188		210	211
40	20.2	84	214		197	177
45	20.6	83	215		187	171
50	21.0	83	217		175	154
55	21.3	80	211		169	144
60	21.7	80	214		167	137
65	22.2	82	223		159	122
75	23.0	82	229		157	113
85	24.0	84	245		151	108
90	24.3	83	243		153	99
105	25.9	87	272		151	89
120	26.9	82	267		135	81
135	27.5	78	265		131	75
150	28.4	74	271		128	70
165	29.2	74	275		125	66
180	29.9	72	278		121	63
195	30.5	69	279	68	116	59
210	30.9	66	274	70	112	56
225	31.3	63	270	72	106	53
240	31.6	60	264	76	106	51
255	32.0	58	264	72	93	44
300	32.4	51	238	67	82	38
345	32.6					
360	32.6					
375	32.6					

change over a considerable period. We prefer, therefore, to ascribe the anomaly to the loss of iodine in the gas phase due to adsorption, iodine being more strongly adsorbed than ethylene iodide.[1] This also accounts

[1] There is also the possibility of ethylene adsorption on glass. Investigators differ in the estimation of the magnitude of this effect.

in part for the prolongation of the induction period, which has the appearance of a steady state, rather than of a slow chemical reaction. The iodine adsorption evidently reaches saturation at low pressures. The rate of reaction is therefore independent of the iodine pressure, and does not appear to be of the second order. But we would expect the apparent incompleteness of the reaction to be more pronounced the greater the activity of the surface, and this is not the case.

TABLE 4

The decomposition of ethylene iodide at 75°C.

Experiment no. 15. No induction period

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$	$k_2 \times 10^6$	$k_3(\sqrt{I_2}) \times 10^5$	$k_2(I_2) \times 10^6$
minutes	*mm.* H_3PO_4					
5	17.9					
10	18.9	125	298		429	595
15	19.7	144	353			
20	20.2	129	319			
25	20.9	132	332			
30	21.6	133	346			
35	22.2	130	346			
40	22.8	129	349			
45	23.6	133	370			
55	24.4	122	350			
70	26.2	122	374			
85	27.5	115	375			
100	28.8	110	385			
115	29.7	104	379			
130	30.5		376	84		
145	31.1		366	87		
160	31.5		348	87		
195	32.1		322	86		
220	32.7		305	88	106	48
250	33 0			86		
310	33.0					
355	33.0					
385	33 0					

We cannot be certain, therefore, if the glass surface itself without iodine is also catalytic to some extent. The introduction of freshly made glass tubing increases the velocity so much that no observation of an induction period is possible. There is not sufficient time for thermal equilibrium to be established and readings on the manometer are unsatisfactory.

There remains the question as to whether the anomalous final pressure is due to some polymerization process. We do not believe this to be the case because of certain independent experiments we carried out. Ethylene iodide was sealed up in a glass vessel and the equilibrium pressure at 35°C.

found to be 22 mm. of mercury. The vessel was then cooled to 16°C. (pressure 5 mm.) and afterwards heated to a much higher temperature, 65°C. It was then allowed to drop to room temperature again, and after some time heated to 35°C. (final pressure 22 mm.). If any irreversible polymerization had taken place during the decomposition at the higher temperature, the initial and final pressures at 35°C. would not have been the same.

The addition of ethylene seems to have a slight accelerating effect on the reaction. It is not easy to explain this, but as a chain mechanism is not

TABLE 5

The decomposition of ethylene iodide at 65°C.

Experiment no. 19. Ethylene (29.2 mm.) added at beginning of reaction. Short induction period

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$	$k_2 \times 10^5$	$k_2(\sqrt{I_2}) \times 10^5$	$k_2(I_2) \times 10^5$
minutes	*mm* H_3PO_4					
5	26 5					
10	27.2					
15	27 2					
20	28 1	(180)	292			
25	28.6	140	230		236	434
30	29 9	(180)	302			
35	30.6	(170)	290			
51	31.0	106	187			
65	33.7	130	237			
80	35.4	126	239			
95	36.9	121	239			
125	40.0	116	251			
140	41.5	114	259			
155	42.4	109	253			
170	43.6	106	258	36		
185	44.0		246	35		
230	45.8		232	37		
245	46 2		226	37	69	27
275	46.8			36		
305	47 0			34		
335	47 0					

altogether improbable for this reaction the ethylene could have some influence in delaying the breaking of the chains at the walls.

For such a chain mechanism we could write:

$$I\ (\text{glass}) + C_2H_4I_2 = I{-}I\ (\text{glass}) + C_2H_4I \quad (1)$$
$$C_2H_4I + C_2H_4I_2 = C_2H_4 + I_2 + C_2H_4I \quad (2)$$
$$C_2H_4I = C_2H_4 + I \quad (3)$$
$$C_2H_4I_2 + I = C_2H_4I + I_2 \quad (4)$$
$$C_2H_4 + I = C_2H_4I \quad (5)$$
$$I\ (\text{glass}) + C_2H_4I = C_2H_4 + I{-}I\ (\text{glass}) \quad (6)$$
$$I\ (\text{glass}) + I = I{-}I\ (\text{glass}) \quad (7)$$
$$I + I_2 = I_3 \quad (8)$$

It seems doubtful if reaction 1 is exothermic, and reactions 2, 4, and 5 are certainly endothermic, and require more energy of activation. Reactions 6, 7, and 8 are the chain-breaking reactions. But the energy of the C—I bond is not known with any certainty, and it would be unwise to generalize about any such chain mechanisms.

The great increase in reaction velocity brought about by the introduction of a larger glass surface is only consistent with the idea that the chains begin at the walls to a greater extent than they end there.

TABLE 6

The decomposition of ethylene iodide at 65°C.

Experiment 21. Enhanced activity of surface. Ethylene 17 mm. No induction period

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$	$k_2 \times 10^5$
minutes	*mm.* H_3PO_4			
5	14.2			
10	23.2	330	685	
13	24.1			
15	24.7			
17	25.5			
20	26.3			
23	27 1			
25	27.9			
30	29.3			
35	30.6			
40	32.1		718	
45	33.3	292		110
50	34.1			112
55	34.8			114
60	35.6			119
75	37.2			125
108	38.5			110
120	38.9			107
165	38.9			

From experiments at 65°C. and 75°C. it should be possible to calculate the energy of activation. But we have never found a satisfactory reproducibility for any one set of values of the velocity constant at either temperature. The catalytic surface does not necessarily remain constant from one experiment to another, and only gross comparisons can be made. But we estimate that the activation energy, calculated[2] from the zero-

[2] This calculation is only possible if the density of the manometric liquid does not vary appreciably, which, in this case, is only approximately correct. We can also calculate the energy of activation from the monomolecular constants. In any case, it is not of a high order.

TABLE 7

The decomposition of ethylene iodide at 65°C.

Experiment no. 22. No ethylene

TIME	PRESSURE	$k_0 \times 10^3$	$k_1 \times 10^5$
minutes	*mm.* H_3PO_4		
3	13.4		
7	18.1		
12	18.9	133	333
17	19.5	150	312
23	20.3	138	358
27	20.8	144	363
35	21.6	135	363
37	22.3	139	
57	25.0	140	
72	26.9	138	
87	29.0	136	
102	30.5	136	
117	31.5	130	
132	32 0		
177	33.2		

TABLE 8

The decomposition of ethylene iodide at 65°C.

Experiment no. 25. Glass capillary tubing in reaction vessel

TIME	PRESSURE
minutes	*mm.* H_3PO_4
5	8.5
7	13.9
10	21.1
12	24.8
17	31.5
22	34.8
27	38.3
32	41.9
37	44.9
42	47.4
48	48.2
59	48.5

Velocity constants indeterminate.

TABLE 9

The decomposition of ethylene iodide at 65°C.

Experiment no. 17. Free iodine at the beginning of reaction

TIME	PRESSURE
minutes	*mm.* H_3PO_4
2	11.8
7	39.2
12	42.2
17	46.2
22	49 9
27	52.8
32	55.7
37	58.3
42	60.0
47	60.8
62	64.2
77	63.8
82	63.8

Velocity constants indeterminate

order constants, is not greater than 12,000 calories. The heat of the endothermic reaction

$$C_2H_4I_2 = C_2H_4 + I_2$$

is 20,000 calories, calculated from the thermal data, assuming the heat of sublimation of ethylene iodide to be 15,000 calories (4), and the heat of combustion of ethylene, 344,000 calories (2).

We hope to explore more deeply the main features of this reaction, particularly as it is affected by the shape of the reaction vessel and the material of the catalytic surface.

We do not wish to express any definite opinion as to the mechanism of the reaction, as it is obvious that there are a number of factors involved.

SUMMARY

The decomposition of gaseous ethylene iodide at 65°C. and 75°C. in a glass vessel seems to be heterogeneous and to a great extent autocatalytic; iodine adsorbed on the glass is a probable catalyst.

There is a short induction period which disappears when traces of iodine are present at the beginning of the reaction, and when the catalytic surface is greatly increased.

The reaction is of zero order after the induction period, and follows higher orders as the pressure diminishes.

A chain mechanism is suggested for the reaction, but this has not yet been completely verified.

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FORMATION OF BENZENE BY THE PHOTOCHEMICAL POLYMERIZATION OF ACETYLENE AT HIGH TEMPERATURES

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The formation of benzene by the photochemical polymerization of acetylene has been reported by Sechi Kato (5), who demonstrated the presence of benzene by means of its distinctive absorption spectrum. Kato claims that the formation of benzene, relative to that of cuprene, is favored by temperatures above 270°C. or by the absorption of light of short wave length. Since these results were in apparent contradiction to the results of a number of other observers (1, 2, 6, 8) who obtained cuprene as the only product of the photochemical reaction, it seemed worth while to repeat Kato's experiments under slightly different conditions. The results of the present work confirm her claim that benzene is formed when acetylene at temperatures above 270°C. is irradiated with ultra-violet light.

APPARATUS AND PROCEDURE

The source and purification of the acetylene were similar to those described by Lind and Livingston (6). The reaction system is represented in figure 1. The reaction vessel was a quartz tube 24.5 cm. long and 2.2 cm. in diameter; it was sealed at the lower end and connected to the line by a graded seal at the upper end. The upper half of this tube was wrapped with a nichrome wire coil, spaced at about half-centimeter intervals. The back and side of the coil were covered by a loosely fitting heavy-walled asbestos shield. The light source, a vertical quartz-mercury arc, was placed opposite the shield at a distance of about 3 cm., and was run "hot" to minimize the probability of a mercury sensitized reaction. The lower part of the reaction vessel was immersed in a mixture of solid carbon dioxide and acetone. The approximate temperature of the acetylene was determined indirectly by measuring the current flowing through the heating coil. These temperature determinations were based upon a series of calibrations, in which a tube with dimensions identical with the reaction vessel was inserted in the heating coil. The upper end of this tube was not constricted but was closed by an asbestos plug through which a thermometer was inserted. The Dewar tube containing the carbon dioxide–

acetone mixture, the asbestos shield, and the mercury arc were arranged as during reaction periods. The temperatures corresponding to current readings were measured from 250°C. to 400°C. The temperature of the irradiated gas was not uniform, but varied from the center to the ends of the heating coil by as much as 50°C. The recorded temperatures all

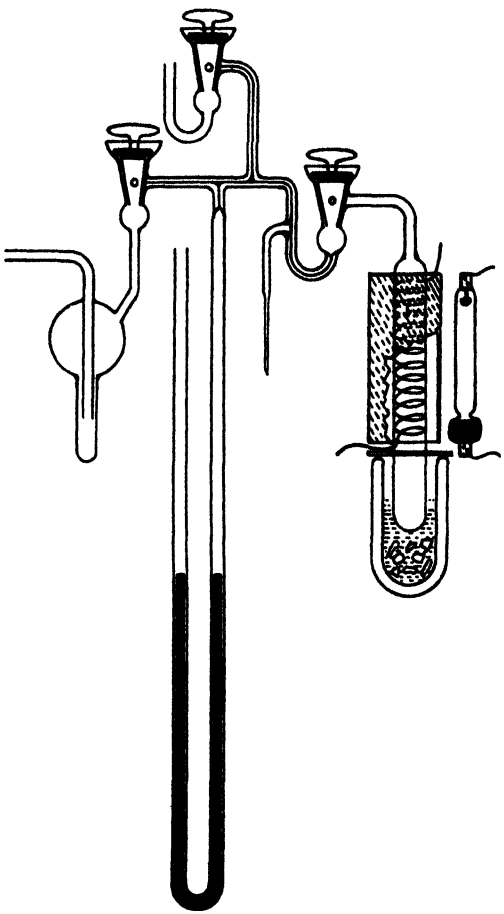

FIG. 1. THE REACTION SYSTEM

correspond to maximum values, and were measured after steady-state conditions had been attained.

Before each experiment air was admitted to the reaction cell, which was then heated to burn out any non-volatile substance. After the system had been evacuated (pressure less than 10^{-4} mm.), sufficient acetylene was admitted to make the pressure approximately 1 atmosphere at the tempera-

ture of the experiment. The pressure was then determined with the whole system at room temperature. The cooling bath was put in place and the heating current started. After sufficient time (about an hour) had elapsed for temperature equilibrium to be attained, the arc was started and was run from three to four and one-half hours. In some experiments an attempt was made to follow the change of pressure during the experiment; in others the manometer was closed off as soon as temperature equilibrium was reached. After each exposure the whole system was allowed to return to room temperature and the pressure was determined and corrected for any change in room temperature.

RESULTS

In all of the photochemical experiments a decrease in pressure was observed and a variety of products was formed. Two of the products were non-volatile solids; one of these resembled cuprene, and the other was a hard dark yellow film, like a film of dried varnish. The cuprene seemed to be evenly distributed and was particularly evident in the irradiated and heated part of the tube. It was insoluble in ether and burned very readily in air. The dark yellow film occurred in the cooler part of the tube, both above the heated zone and in the bottom of the tube. When heated in vacuum it charred, but did not sublime. It was partly soluble in ether, coloring the ether dark yellow; it formed a dense and adherent coating which burned in air only with difficulty. A small quantity of a volatile liquid was always found frozen in the bottom of the tube. This liquid was yellow and viscous. When the bottom of the tube was immersed in liquid air there was no detectable residual pressure, which indicates the absence of hydrogen and methane. No other attempt was made to isolate gaseous products.

While the experimental method did not allow exact measurement of the rate of change, it was demonstrated that the rate was initially at a maximum and became negligible after three or four hours. This was probably due to the absorption of the incident light by the cuprene which accumulated on the walls of the tube. The decrease in pressure varied from 3.5 per cent for a 3-hour exposure at 270°C. to 9.3 per cent for a 4.5-hour exposure at 375°C. These changes are apparently much greater than those which would have been obtained at room temperature under otherwise similar conditions. No measurements were made at temperatures below 270°C. or above 376°C.

That the reaction was truly photochemical and not thermal was demonstrated by two independent blank experiments. In one the quartz reaction vessel was replaced by a Pyrex tube of similar dimensions. All other conditions were identical with those used in the photochemical experiments; at the end of two and one-half hours there was no measurable

change of pressure nor visible accumulation of products. In another experiment the quartz tube was used but the arc was not started. The temperature was maintained at 350°C. for 4 hours, at the end of which time there was no evidence of any reaction having occurred.

The following experiments were performed in an attempt to determine the nature of the volatile liquid products. The liquids were frozen with carbon dioxide–acetone mixture and the gas was pumped off. A capillary side tube was then immersed in liquid air and the more volatile liquids were allowed to distil over. The distillate always consisted of a few cubic millimeters of a non-viscous liquid, which was clear or faintly yellow (depending on the time allowed for distillation). After one of the experiments, which was performed at 345°C., the capillary side tube and manometer were sealed off from the reaction vessel, and the side tube was immersed in an acetone bath which was cooled with solid carbon dioxide. The vapor pressure measurements given in table 1 were made. While

TABLE 1

Vapor pressure of the distillate

TEMPERATURE OF THE BATH	VAPOR PRESSURE OF DISTILLATE	VAPOR PRESSURE OF BENZENE (4)
degrees C.	*mm.*	*mm.*
−24 to −25	4.3	3.6
−19 to −20	6.6	5.5
−14 to −15	10.1	8.2
−9 to −10	14.2	12.1
−5.5 to −6	18.6	16.1

the vapor pressure values given are not in sufficiently close agreement with the published values for benzene to make it possible to identify the distillate as benzene, it does seem probable that the distillate is a mixture consisting chiefly of benzene. Under the conditions of the experiment the distillate appeared to melt over the range −9°C. to −15°C. At temperature above −5°C. the volume of the liquid was very small and it had a distinct yellowish color.

To obtain definite evidence of the presence (or absence) of benzene, the distillate was transferred in vacuum to a quartz absorption cell, which was 5 cm. long and was equipped with a side tube. The absorption spectrum was photographed with a Steinheil spectrograph, using a hydrogen arc as a light source (7). When the cell was at room temperature a continuous absorption set in at about 2225 A.U., with a region of partial transmission between 2140 and 2270 A.U. In the region between 2225 A.U. and 2650 A.U. (the long wave length limit of the spectrograph), several bands were noticeable which coincided with the benzene bands recorded by

Henri (3). When the side tube of the cell was maintained at −37°C. the continuous absorption vanished; a regular series of bands was noticeable between 2275 and 2603 A.U. Fourteen of these bands were identified as benzene bands. We may conclude from these results that the distillate consisted of benzene and some less volatile substance which exhibited a continuous absorption in the ultra-violet.

CONCLUSIONS

It is noteworthy that the products of the photochemical polymerization of acetylene at high temperatures resemble those of the thermal polymerization (9) much more nearly than they do those of the low temperature photochemical reaction. At the present time any attempt to give a detailed analysis of the reaction mechanism would be premature. It seems probable that not all of the detailed analysis of Kato (5) will prove to be correct. Her assumption that the apparent continuum on the long wave length side of the banded absorption corresponds to a region of predissociation seems unlikely. It is quite possible that the continuous absorption was due to some impurity present in the acetylene. It is very probable that the solid condensate which is formed in the photochemical reaction is a true polymer rather than the dehydrogenated product $(C_7H_6)_n$, assumed by Kato. In the absence of any information on the intensity of the light absorbed at the different frequencies used in Kato's experiments, it is difficult to decide whether her conclusion that light of short wave length favors benzene formation is justifiable.

SUMMARY

The photochemical polymerization of acetylene at temperatures above 270°C. has been studied qualitatively. In confirmation of the results of Kato (5), benzene has been identified as one of the reaction products.

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THE ADSORPTION OF THE VAPORS OF CERTAIN DICHLORO HYDROCARBONS BY ACTIVATED CHARCOAL. IV

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In the previous papers reports have been made of studies of the adsorption of the vapors of methane and its chlorine derivatives (6), and of ethyl, propyl, isopropyl, *n*-butyl, and *tertiary*-butyl chlorides (7). Since all of these adsorptions have been made on samples from the same stock of acid-washed, ash-free, steam-activated charcoal, the results should be comparable and significant.

The extremely uneven nature of the charcoal surface gives rise to a great variation in the nature of the adsorption forces emanating from the surface atoms. The surface is composed chiefly of capillary pores, cracks, and fissures; the surface atoms may be those of unbroken benzene rings, exposed carbon chains, and projecting peaks of single carbon atoms. Obviously, the degree of unsaturation of the surface forces, and hence the intensity of the adsorption forces, will be greatest for the projecting atoms. The influence of the fine capillary structure upon adsorption is shown by the calculations of Magnus (3). Assuming that the attractive force exerted upon a molecule decreases with the sixth power of the distance from the surface element, he finds that a molecule situated in a hemispherical concavity of about equal size is attracted about three times more strongly than by a plane surface.

The forces operative in the adsorption of vapors and gases at charcoal surfaces may be those of simple adsorption due chiefly to van der Waals forces, or they may be more of an electrical nature. The latter follows from the fact that the electrical field at a distance of 1 A.U. from a surface atom is of the order of 1×10^9 volts per centimeter. This field is capable of orienting and attracting vapor molecules possessing permanent dipole moments; it is capable not only of increasing dipole moments already present, but also of inducing dipoles in neutral molecules and quadripoles. The induced dipole will be greater, the greater the ease of deformation of the electronic orbits of the constituent atoms. In this way many nonpolar molecules may become as highly adsorbed as those of a highly polar nature.

In the interpretation of the previous results we have assumed that the

attraction between the surface of the adsorbent and the vapor molecules is largely influenced by an attraction for some particular atom or group of atoms within the molecule adsorbed. It has been assumed that the chlorine atom plays the dominant rôle in the adsorption of the alkyl chloride vapors. If our assumption is correct, we should expect that for any alkyl chloride series the number and position of the chlorine atoms in the molecule, as well as the shape and volume of the molecule, should be important factors in the intensity of the adsorption and in the relative amounts of the different vapors adsorbed under corresponding conditions. With the normal compounds, the chlorine atom should be attracted toward the surface of the adsorbent, with the hydrocarbon chain extending outward into space. The surface cover-power of all normal alkyl chloride molecules should be the same.

On the basis of the assumption that adsorption takes place through the chlorine atom, the intensity of the adsorption should increase with the number of chlorine atoms in the molecule. If two chlorine atoms are present, the intensity and magnitude of the adsorption will depend upon their position. If the two are joined to the same carbon atom, the molecule will probably be adsorbed on a single point or elementary space, unless the points are sufficiently close together to attract the chlorine atoms separately. On the other hand, if the two chlorine atoms are attached to two different carbon atoms, the molecule should lie flat upon the surface. The surface covering power of these molecules will be greater than for those with the chlorine atoms attached to the same carbon atom.

The present paper gives a brief statement of the results obtained in a study of the adsorption of the vapors of ethylene, ethylidene, propylene, and trimethylene chloride vapors.

The dichloro compounds used were Eastman's products of highest purity. They were further purified by means of a special fractional distillation apparatus (2, 8). The liquids finally used were fractions of 75 to 100 cc. collected over a range of 0.01° to 0.10°C. and having the correct boiling points.

The apparatus and the technique employed were the same as that described in the previous papers (6, 7). It should be stated that before use each sample of charcoal was first outgassed at 525°C., then flushed one or more times with the vapor to be adsorbed, and finally outgassed at 525°C.

DISCUSSION

The results obtained are collected in tables 1 to 4. In these x/m is the number of cubic centimeters of vapor (N.T.P.) adsorbed by one gram of charcoal under the equilibrium pressures p (in millimeters). The 0°C. and 40°C. isotherms were carried up to the saturation pressures of the

pure liquids at these temperatures. The equilibrium pressures at the higher temperatures were limited to the saturation pressures at 50°C.,—the temperature of the air bath. Each pressure recorded is the mean of three or four readings taken at 30-minute intervals during which the increase in pressure did not exceed the limits of accuracy of the large precision cathetometer. Duplicate series on entirely different samples of char-

TABLE 1

The adsorption of ethylene chloride vapor by charcoal at various temperatures

At 0°C.														
p.....	0.15	0 25	0.35	2.03	5.78	11 45	17 70	20 61	20 76					
x/m. .	30 05	57.42	72.79	97.51	103.72	109 60	114 25	117 71	124 68					
At 40.00°C.														
p.....	0.15	0.25	0 30	0 45	0 75	2 13	6 75	16 88	40 80	73.21				
x/m....	8.95	17 78	26 51	43 49	64 37	79 12	88 06	93 10	97 89	102 14				
p.....	105.38	138 98	146.18	149.25	152 58	152 88	153 07							
x/m....	106 52	110.13	110 82	110.99	112 14	112 72	113 83							
At 63 96°C.														
p.....	0.15	0.50	0 80	1 34	2 38	4 42	10 82	26.06	53 61	99.37	135 16	139 88	142 06	
x/m...	11.86	26 06	38 31	49 61	61.05	69.13	78 10	84 20	88 05	91 36	93 17	93 69	95 16	
At 79.50°C.														
p...	0.50	1.00	1.73	3.12	5.60	11 05	26.61	67 34	103 61	142 06	179 32	193 24	196 32	
x/m.	16.68	29.20	41 36	52 37	61.51	70 92	79.92	86 22	88 83	90.61	91 01	92 43	92 73	
At 99 48°C.														
p..... .	1.24	2.68	5 80	9 27	18.43	39 00	72.79	122 93	165.30	186 80	220 30	222 33		
x/m.....	19.18	33 47	45.13	53.22	64 18	73.26	79 15	83 11	84.93	85 62	87 21	89 62		
At 136.20°C.														
p.....	3 47	10.26	18.73	32 84	62.43	115 30	141.28	190 37	195 47					
x/m....	16 45	32.15	41.87	52.03	61.71	70 15	72 27	75 31	76.20					

coal showed that pressure equilibria are easily reproducible at all temperatures and pressures. As with the monochloro vapors, the dichloro vapors decompose with measurable speed at about 180°C.

In his development of a quantitative theory of adsorption, Langmuir (1) has deduced six relations, each applicable to definite limiting conditions. These relations satisfy the different possible configurations of the surface atoms and the number of molecules which each elementary space may ad-

sorb. The simplest of these involves the simple adsorption of vapor molecules on a plane surface possessing only one kind of elementary space, and each space capable of holding only one adsorbed molecule. For this condition the amount of gas adsorbed by one gram of charcoal is given by the relation,

$$\frac{x}{m} = \frac{abp}{1 + ap}, \quad \text{or} \quad \frac{p}{x/m} = \frac{1}{ab} + \frac{p}{b} \tag{1}$$

TABLE 2

The adsorption of ethylidene chloride vapor by charcoal at various temperatures

At 0°C.											
p.....	0.25	0.50	1.50	4.86	10.90	22.55	38.25	49.50	57.92	66.00	70 66
x/m.....	28.89	57.48	85.50	95.12	98.87	103.05	107.82	110 48	113 66	116 48	120 53
At 40.00°C.											
p.....	0.25	0.70	1.70	4.67	11.66	24.77	52.12	125.43	179.18	248 18	319 21
x/m.....	24.38	43.24	59.43	70.99	78 48	83.14	87.08	91.48	93.77	96 85	100.11
At 64.00°C.											
p.....	0 60	2.08	5 00	10.60	22 89	47.37	102 57	107.59	255 33	398.98	479.74
x/m.....	24.20	42.53	56.62	66.23	73 88	79.30	84 06	86.98	89 01	91.60	93.05
At 79.50°C.											
p.....	0.95	3.37	8.47	21.60	50.24	89.44	164.56	263.46	407.30	497.80	505.51
x/m.....	17.01	35.68	51.39	64.99	74.02	78.87	83.54	85.48	87.87	89.27	91 71
At 99.50°C.											
p.....	2.08	6.64	17.19	36.32	68.78	111.20	169.96	237.94	367 22	493.86	504.57
x/m.....	20.01	36.41	50.35	61.04	68.14	72.77	76.11	78.52	80.54	82.41	85.20
At 136.65°C.											
p.....	3.86	13.87	28.00	53.51	90.78	141.17	274.41	356.96	478.16	565.12	
x/m.....	15.47	27.87	36.14	43.98	50.55	55.68	65.50	64.68	66.89	68.52	

Here, $1/b$ is the slope of the straight line plot and $1/ab$ is the intercept on the ordinate at zero pressure.

Charcoal, however, is a highly porous solid with a variety of projecting points, crags, crevices, capillaries, and minute elementary surface spaces, all of which may be unlike. The relation which Langmuir has derived for amorphous adsorbents represents a complicated function whose exact form can not be determined with our present knowledge of the nature of charcoal surfaces.

Since the plots of the log x/m against the log p show that the Freundlich

equation does not hold for any of these vapors, we have chosen the only alternative possible and have plotted our isotherms in accordance with equation 1. These isotherms for the four dichloro compounds are shown in figures 1 and 2. Within the pressure range indicated by the experimental points the adsorption relations for these vapors are satisfactorily expressed by the Langmuir equation. At lower pressures than those indicated the values of $p(x/m)$ appear to diminish rapidly with diminishing pressure and the simple adsorption equation 1 no longer applies.

TABLE 3

The adsorption of propylene chloride vapors by charcoal at various temperatures

At 0°C.											
p	0.10	0 20	0 30	0.40	2 03	5 75	8 23	12 20	12 88		
x/m	36 14	53 98	67.61	76.94	84 17	90 63	93.49	96 49	100 15		
At 40.00°C.											
p	0 25	0 40	1 59	6 06	12 61	24 27	42 98	56 58	65 12	79 02	84 53
x/m	36 82	57 50	72 10	78 61	80 67	83 51	86 83	89 08	90 65	92 99	95 40
At 63.88°C.											
p	0 35	1 30	7 58	26.70	60 95	91 32	124 37	134.48			
x/m	32 58	57 61	69 18	74.36	77 53	79.64	81.68	84 20			
At 79.20°C.											
p	0.30	1.00	3.45	8.00	21.90	29.15	45.00	105.70	138.30		
x/m	22 97	44.03	56 45	62 09	66 99	68.18	69.76	73 14	75.72		
At 99.22°C.											
p	0 55	2.58	6.89	15.26	40 68	85.28	125 56	136.80			
x/m	25 78	44 07	54.80	61.33	66 92	70.35	72.04	74 96			
At 136.20°C.											
p	2.03	7 33	16 65	35.23	67 60	105.65	136.60	138 15			
x/m	21 74	34 46	42 81	49.62	54 09	56.91	58.62	60.35			

McBain and Britton (4) have studied the adsorption of nitrous oxide, ethylene, and nitrogen by charcoal at different temperatures and under pressures up to 40 and 60 atmospheres. They find that equation 1 adequately expresses the adsorption relations throughout the whole pressure range. McBain, Lucas, and Chapman (5) find that a plot of $(p/p_0)/(x/m)$ against the relative humidity, p/p_0, gives a straight line throughout the pressure range studied for toluene, hexane, octane, decane, acetone, and acetic acid vapors. It appears to fail, however, for methyl alcohol

vapor at low pressures, and the authors attribute the deviations to the presence of residual impurities.

The study of the adsorption of vapors of the kind here used and the possibility of drawing definite conclusions as to the influence of the structure and complexity of the vapor molecules upon adsorption is hampered by the fact that the study is limited to temperatures at which liquefaction is possible. This is particularly true at the lower temperatures employed at which the forces operative in condensation may coëxist along with those

TABLE 4

The adsorption of trimethylene chloride vapor by charcoal at various temperatures

At 0°C.										
p	0.05	0.10	0.15	0.30	1.50	3.12	3.72	3.77	3.82	
x/m	23.82	50.45	66.42	81.35	89 67	94.15	98.73	109.11	119.83	
At 40.00°C.										
p	0.10	0.15	0.35	3 62	8.30	15.75	23.80	26.75	31.02	33.00
x/m	21.39	42.90	63.18	78 71	81.77	85.08	88.23	89.24	90.51	92.00
At 63.85°C.										
p	0.15	0.25	0.50	3.32	12.34	19.32	36.96	45 24	50 05	
x/m	27.64	44.57	57.72	72.77	77.91	79.82	82.96	84.23	85.98	
At 79.10°C.										
p	0.15	0.35	0.90	2.23	7.18	15.41	36.07	47.57	50.15	
x/m	25.90	42.93	54.35	63.93	69.99	73.32	76 74	77.94	79 15	
At 99.50°C.										
p	0.30	0.75	2.38	6 65	19.32	40.73	50 44			
x/m	24.07	41.38	55.71	65.27	72.03	75.52	77.35			
At 136.20°C.										
p	0.80	3.27	8.67	18.33	35.58	49.95				
x/m	20.36	36.42	48.38	56 43	61.95	64.56				

of adsorption. The orientation and adsorption of the vapor molecules is opposed by thermal agitation. Since the amount of vapor adsorbed diminishes as the temperature is raised, there should be for each vapor a critical temperature above which adsorption is impossible. A satisfactory comparison of adsorption magnitudes on a given surface can only be made when the thermal energies of the vapor molecules are equal.

Although the critical adsorption temperatures may not be identical with their critical temperatures, we have assumed nevertheless that the

boiling points of the liquids are corresponding adsorption temperatures. We have assumed also that the variation of the adsorption with the temperature is linear through the narrow interval between the experimental isotherms just above and below the boiling points. In this way we have

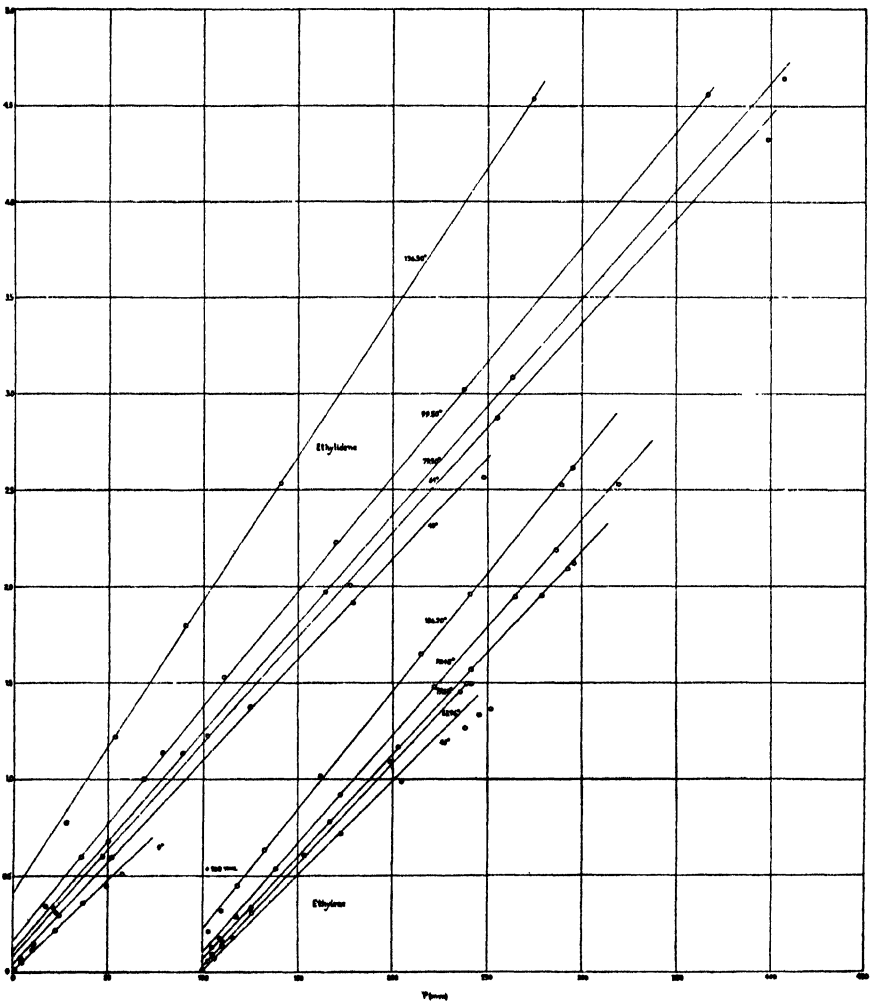

FIG. 1. THE LANGMUIR ADSORPTION ISOTHERMS FOR ETHYLENE AND ETHYLIDENE CHLORIDE VAPORS AT VARIOUS TEMPERATURES

calculated the isotherm data of table 5 for the vapors of all of the chlorine substituted compounds studied thus far. The natural boiling point isotherms plotted from these data are shown in figure 3. The relative amounts of the different vapors adsorbed at their boiling points should be significant.

A study of figure 3 shows certain definite regularities. Under an equilibrium pressure of 1 mm. ethyl chloride is more highly adsorbed than is methyl chloride, and both are more highly adsorbed than *n*-propyl and *n*-butyl chloride. Of the latter two the propyl chloride is the more highly adsorbed. At still lower pressures the order of increasing adsorption is methyl, ethyl, *n*-propyl, *n*-butyl. This is exactly the order of their respec-

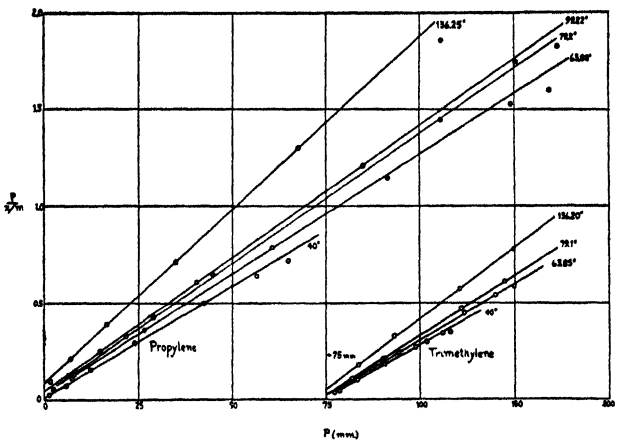

FIG. 2. THE LANGMUIR ADSORPTION ISOTHERMS FOR PROPYLENE AND TRIMETHYLENE CHLORIDE VAPORS AT VARIOUS TEMPERATURES

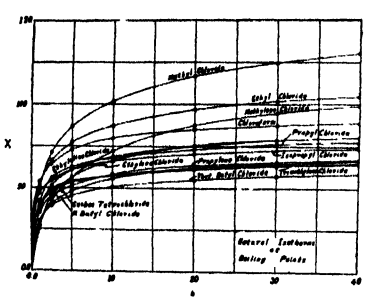

FIG. 3. THE NATURAL ISOTHERMS OF VARIOUS CHLORINE DERIVATIVES OF THE ALIPHATIC HYDROCARBONS AT THEIR BOILING POINTS

tive molecular weights, boiling points, and dipole moments. At higher pressures the order of adsorption is exactly reversed; methyl chloride is the most highly adsorbed and butyl chloride the least.

The isopropyl and *tertiary*-butyl chloride vapors, as we might expect, from their greater surface covering power, are less adsorbed at all pressures than the corresponding normal vapors.

Chloroform is more highly adsorbed than methyl chloride below 1.3 mm.

and more highly adsorbed than methylene chloride below 17 mm. From the trend of the isotherms we may infer that carbon tetrachloride is more highly adsorbed than chloroform at very low pressures. At higher pressures, however, the order of increasing adsorption is that of decreasing molecular volume, namely, $CCl_4 < CHCl_3 < CH_2Cl_2 < CH_3Cl$.

Ethylidene chloride is more highly adsorbed than ethylene chloride up to 19 mm. Above this pressure they are adsorbed to practically the same extent at all pressures. The greater adsorption of the lower boiling ethylene chloride at the lower pressures is interpreted as being due to the fact

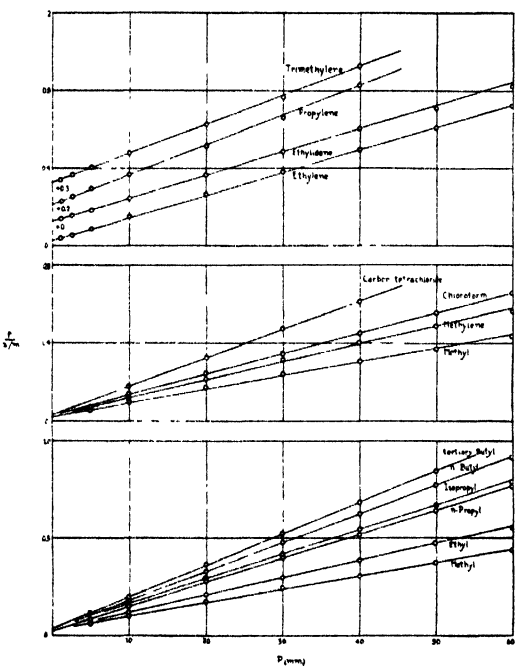

FIG. 4. THE LANGMUIR ADSORPTION ISOTHERMS OF VARIOUS CHLORINE DERIVATIVES OF THE ALIPHATIC HYDROCARBONS AT THEIR BOILING POINTS

that the two chlorine atoms are attached to the same carbon atom. Thus, the attraction for the vapor molecule is increased, and since the radical extends outward, more molecules may be adsorbed.

Ethylene chloride is less adsorbed than propylene chloride at pressures below 2.5 mm.; it is less adsorbed than trimethylene chloride below 1.7 mm. The latter, in turn, is less adsorbed than propylene chloride below 2.5 mm. Above the pressures indicated the order of adsorption is: ethylene > propylene > trimethylene. This is exactly the order to be predicted from the respective surface covering powers of the three vapors on

the assumption that the adsorption is due to the attraction of the surface forces for the chlorine atoms.

While we have discussed the adsorption with respect to four series of chlorine substituted vapors, the relative adsorbability of the vapors of the different series may be easily noted from figure 3. In general, it may be stated that for any one of the series of vapors, the higher boiling, heavier molecules are most highly adsorbed at low pressures. The adsorption of these quickly approaches a maximum and then increases but slightly with further increase in pressure. At relatively high pressures the more simple the molecule is, the greater is the tendency of the adsorbent to adsorb additional vapor as the pressure is increased.

We have plotted the boiling point isotherms corresponding to the simple adsorption equation of Langmuir. These are shown in figure 4. Because of the approximate equality of the adsorption magnitudes of the ethylene and ethylidene chloride vapors, and of those of propylene and trimethylene chloride, it was necessary to displace the plots upward by definite space intervals.

Within the limits indicated by the experimental points, the Langmuir equation for simple adsorption on a plane surface adequately expresses the adsorption for the chlorine compounds studied. At lower pressures the values of $p/(x/m)$ fall rapidly below the straight line plot. This is not surprising since the Langmuir equation (1) applies only to adsorption on a plane surface. Charcoal surfaces are exceedingly irregular; they are made up of points, edges, and capillaries, and the atoms of each possess adsorption forces of widely varying intensity. Upon exposing the gas-free charcoal surface to a vapor it is the more intense forces emanating from the surface atoms that are first saturated. Only when these points have become covered with vapor molecules will the adsorption approximate in nature that on a plane surface. Then and only then should the simple adsorption equation apply to the adsorption of vapors on charcoal surfaces.

The heats of adsorption of the four dichloro vapors studied in this research were calculated from the slopes of the isosteres. The heats of adsorption obtained are: ethylene chloride, 11,500 calories; ethylidene chloride, 10,965 calories; propylene chloride, 13,160 calories; trimethylene chloride, 13,700 calories. Since the heats of adsorption of these vapors have not been determined experimentally, we can only state that the above values are probably of the right order of magnitude. In general, however, it has been found that heats of adsorption calculated from the isosteres are usually lower than those experimentally obtained.

SUMMARY

The adsorption of the vapors of ethylene chloride, ethylidene chloride, propylene chloride, and trimethylene chloride on charcoal has been studied

at several temperatures between 0°C. and 136°C. Within the pressure range employed, the adsorption magnitudes are satisfactorily expressed by the simple Langmuir equation for adsorption on plane surfaces.

Both the natural and the Langmuir isotherms have been plotted for these vapors and for the chlorine derivatives previously studied at temperatures corresponding to the boiling points of the pure liquids. The Langmuir equation applies for the pressure range studied. The Freundlich equation does not hold for any of the vapors.

For any one series the amount of vapor adsorbed at very low pressures is always greatest for that vapor having the greatest molecular weight, the largest molecular volume, and the highest boiling point; it is least for the simpler, lower boiling liquids. Similar relations obtain with increase in the number of chlorine atoms within the molecule. At higher pressures the order of the adsorption magnitudes is exactly reversed.

The influence of the number and position of the chlorine atoms has been determined.

The heats of adsorption of the vapors have been calculated from the slope of the isosteres.

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THE EFFECT OF TEMPERATURE ON THE VISCOSITY OF BINARY MIXTURES WITH ABNORMAL VISCOSITIES

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The effect of temperature on the abnormal viscosities of certain binary mixtures has received both experimental and theoretical consideration. In a general way, experimental evidence indicates that at higher temperatures the abnormality diminishes and the viscosity of the mixture tends to follow the law of mixtures. Further, the constancy or variation in the composition at which the abnormality occurs, when the temperature is changed, has been used to determine the cause of this abnormal behavior. Most cases can be explained on the assumption of (1) compound formation, (2) complex formation, (3) association, and (4) dissociation.

Drucker and Kassel (3) in their investigation of systems with maximum viscosities, find in all cases investigated that an increase in temperature decreases the sharpness of the maximum point. Kurnakov and Krotkov (6) in an investigation of some twenty mixtures, find that not only is the sharpness of the maximum point decreased with increasing temperature, but also there is a shift in the composition of the maximum viscosity mixture in the direction of higher concentration of the more viscous component. De Carli (2) and Errera (5) report similar behavior in systems they have investigated.

Dunstan and Thole (4) have investigated the effect of temperature on the viscosity maximum shown by the system water–acetic acid, up to temperatures of 30°C. Taakalatos (7) has investigated the system pyridine–acetic acid over about the same temperature range. J. Wagner (8) has studied the system nitrobenzene–*n*-butyl alcohol. The first two systems mentioned show a maximum viscosity point, the last a minimum. In the data reported on these systems there appears to be little if any shift in the composition of the mixture having the maximum viscosity at higher temperatures.

This paper deals largely with an extension of the existing data on these three systems to higher temperatures.

APPARATUS

Drucker type viscosimeters were used. Pressure–time products were checked for each viscosimeter.

The vapor thermostat, suggested by Daniels, Mathews, and Williams (1) was used to secure the various constant temperatures. Carbon disulfide (b.p. 46.2°C.), acetone (b.p. 56.5°C.), methyl alcohol (b.p. 66°C.) and benzene, (b.p. 80.38°C.) were used in the vapor thermostat.

Vacuum jacketed 10-cc. pycnometers, calibrated with distilled water, were used for density measurements.

All thermometers used were carefully checked against thermometers calibrated by the U. S. Bureau of Standards.

MATERIALS

Freshly boiled, twice distilled water was used in preparing the acetic acid–water mixtures and for standardizing the pycnometers and viscosimeters.

A standard C.P. brand of glacial acetic acid was purified by repeated fractional crystallization.

Commercial grades of pyridine, nitrobenzene, and *n*-butyl alcohol were purified by repeated fractional distillation.

METHOD

Mixtures of the two components, with composition expressed in mole per cent, were made up covering the entire range of composition. Densities of the various mixtures were determined from room temperature to about 80°C., using the vapor thermostat. The time of flow for an equal volume of water or mixture was measured over this temperature range. The same volume of liquid was used in the viscosimeter at all temperatures. Volumes of water or mixture were brought into the viscosimeter after having been previously brought to the desired temperature. Relative viscosities of mixtures were calculated from densities and times of flow of the mixtures and water at corresponding temperatures. Absolute viscosities were calculated from relative viscosities, using density and viscosity data for water from the International Critical Tables.

EXPERIMENTAL RESULTS

Tables 1, 2, and 3 and figures 1, 2, and 3 show the viscosities of the three systems over a temperature range from 35°C. to 75°C. in intervals of 10°C. These data, at even temperatures, were taken from large scale graphs of the experimental values for temperatures obtained with the vapor thermostat.

Reference to figure 1 shows that in the case of the acetic acid–water system, the composition of the mixture having maximum viscosity remains practically constant at 55 mole per cent acid. Figure 2 shows this also to be the case of the system pyridine–acetic acid. The viscosity isotherms

TABLE 1

The viscosity of acetic acid–water mixtures at various temperatures

ACETIC ACID	VISCOSITY × 10^3 C.G.S. UNITS					
	At 35°C.	At 45°C.	At 55°C	At 65°C.	At 75°C.	At 80°C.
mole per cent						
100	10.12	8.53	7.46	6.60	5.82	5.40
80	15.24	12 26	10.30	8 77	7 47	6.92
60	18.10	14.33	11 63	9.74	8.20	7.52
55	18 48	14.50	11.82	9 82	8.28	7.60
50	18.47	14.49	11.80	9 80	8.27	7.59
40	17.68	14.03	11 32	9 32	7.83	7.24
20	13.03	10.95	9 00	7.60	6.48	5.95
0	7.18	5.97	5 07	4 36	3 80	3.57

TABLE 2

The viscosity of pyridine–acetic acid mixtures at various temperatures

PYRIDINE	VISCOSITY × 10^3 C G S UNITS					
	At 35°C	At 45°C	At 55°C	At 65°C.	At 75°C	At 80°C
mole per cent						
100	7 80	6 60	5.88	5 35	4.84	4.65
80	10 52	8.96	7 88	6 82	6 20	5.83
60	12.70	10 70	9 20	7.80	7.10	6.70
40	19 28	15.20	12 65	10.80	9 35	8.73
30	25.50	19.85	15 80	13.05	10 93	10.00
25	28 87	22 00	17.55	14.30	11.75	10.70
20	31.70	23 80	18.60	15.00	12 57	11.15
15	32 00	23.50	18 20			
0	10.12	8 53	7 46	6.60	5 82	5.40

TABLE 3

The viscosity of nitrobenzene–n-butyl alcohol mixtures at various temperatures

NITROBENZENE	VISCOSITY × 10^3 C G S. UNITS					
	At 35°C.	At 45°C	At 55°C	At 65°C.	At 75°C.	At 80°C
mole per cent						
100	16.01	13 27	11.24	9 80	8 78	8 27
95	14 53	12.52	10.81	9 46	8 47	8.05
90	14 03	11.96	10.35	9 06	8 10	7.70
80	13.50	11.47	9.86	8.54	7.60	7 22
60	13.39	11.09	9.31	8.02	7.06	6 65
40	14.11	11.28	9.49	8.07	6.87	6 33
20	15.80	12.70	10.13	8.36	7.11	6 60
0	20 24	15 53	12.23	9 94	8.10	7.33

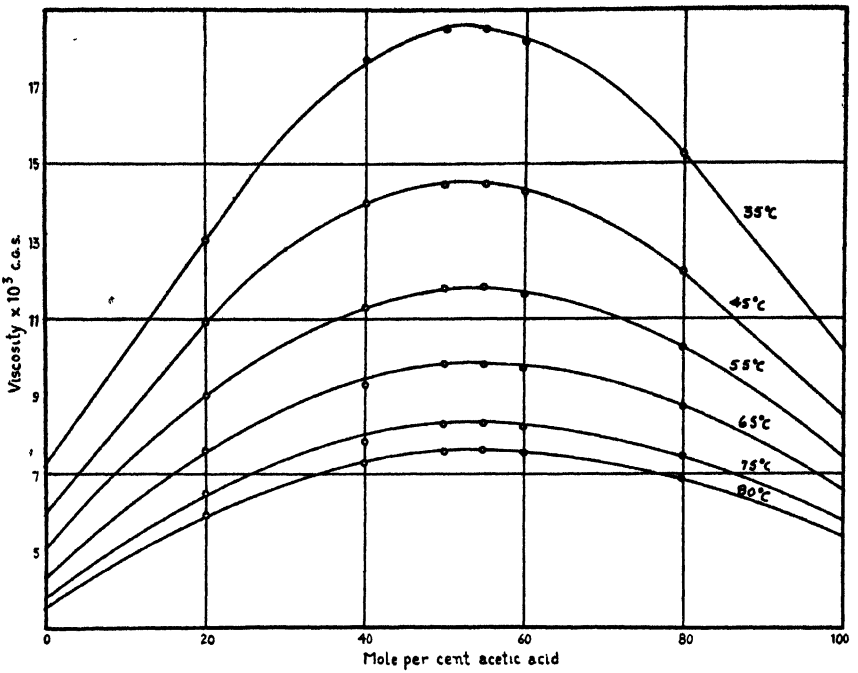

FIG. 1. VISCOSITY ISOTHERMS FOR ACETIC ACID–WATER MIXTURES

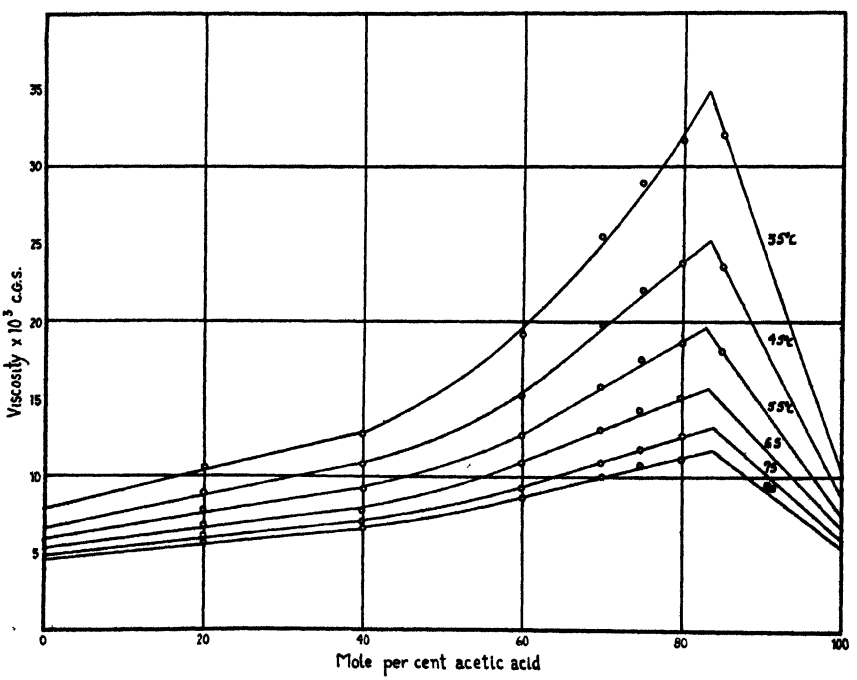

FIG. 2. VISCOSITY ISOTHERMS FOR PYRIDINE–ACETIC ACID MIXTURES

flatten considerably at the higher temperatures, but the maximum is clearly in evidence at a fixed composition in each case.

The viscosity isotherms for the system nitrobenzene–*n*-butyl alcohol show a minimum present for all temperatures investigated. In contrast with the two preceding cases, as the temperature is raised, this system shows a marked and quite regular shift in the composition of the mixture having minimum viscosity. The isotherms are quite flat at the higher temperatures.

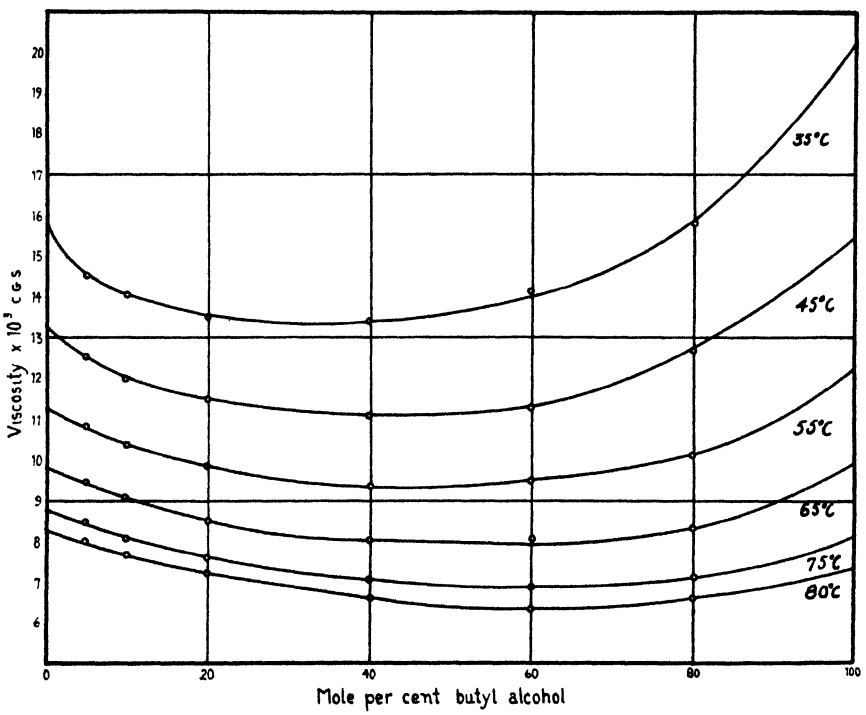

FIG. 3. VISCOSITY ISOTHERMS FOR NITROBENZENE–*n*-BUTYL ALCOHOL MIXTURES

SUMMARY

The effect of temperature on the composition of mixtures having maximum or minimum viscosity has been studied for the systems acetic acid–water, pyridine–acetic acid, and nitrobenzene–*n*-butyl alcohol.

The first two systems show the maximum to occur at fixed compositions for temperatures as high as 80°C. The third system shows a minimum point, occurring at varying compositions, depending on the temperature.

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ELECTROKINETIC POTENTIALS AND MINERAL FLOTATION[1]

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There has been much speculation as to the rôle which electrostatic charges play in ore flotation (2, 7, 9, 10, 16). The attempts to determine these charges experimentally have yielded various methods as well as various results. The majority of these measurements have dealt with the electrokinetic potential (ζ), while there is some more recent work dealing with thermodynamic potential of galena immersed in various solutions (15). In studying potentials these two must not be confused (11). Ince (14) made use of a Burton cataphoretic tube. Burtsch (5) investigated the problem by means of electroösmosis. Bull (3) utilized the Dorn effect to study the potentials on galena particles.

EXPERIMENTAL

We employed cataphoretic technique in our studies and made use of a modification (4) of a micro cell developed by Buzágh (6). It consisted simply of a groove 1 mm. deep, 1.25 cm. wide and 16.5 cm. long cut in a strip of plate glass which had two small holes ground into it on each end to act as an outlet and inlet for the suspension of ore particles. A thin cover glass was sealed over this groove with sealing wax. Cork slivers were inserted at either end of the groove to a certain distance to prevent contamination of the contents of the cell. Copper electrodes consisting of copper wire in a saturated sodium nitrate–agar agar gel were slipped in behind the cork dams and the whole sealed in place. In accord with Smoluchowski's (17) treatment the measurement of the velocity of the particles was made one-fifth the distance from the top and bottom. The distribution of velocities with the distance from the bottom was not a

[1] This research was made possible by a grant from the Graduate School of the University of Minnesota. The experimental work was done in the Division of Agricultural Biochemistry of the University of Minnesota. Part of the discussion was furnished by Dr. N. W. Taylor, Chairman of the Department of Ceramics, Pennsylvania State College.

completely symmetrical parabola as demanded by theory, the particles one-fifth the distance from the top always traveling a little more slowly than those at the corresponding position at the bottom. The readings recorded in this paper are those obtained at one-fifth the distance from the bottom of the cell.

In making this study of the effect of electrolytes on the electrokinetic properties of galena, we tried to follow as closely as possible the condition of the flotation experiments as conducted by Taylor and Bull (18) in order to discover any simple relationship between the toxic effect of the cations and the electrokinetic potential. The $M/10$ solutions of electrolytes were prepared from pure chemicals. The hydrochloric acid and nitric acid solutions were carefully standardized. The pH values of the solutions noted on the graph were determined by means of the quinhydrone–platinum electrode.

The galena ore, a 300-g. lot as pure as could be obtained,[2] was ground in an agate mortar (diameter of particles in cell varied from 3μ to 25μ) and the whole thoroughly mixed and stored in closed bottles out of direct contact with air. The other minerals used, pyrite, quartz, anglesite, sphalerite, cerussite, and rhodochrosite were the purest naturally occurring ores obtainable.

The technique of the measurement was to add 0.574 g. of galena or 0.201 g. of quartz, as the case might be, to 500 cc. of the solution investigated. This was shaken and allowed to stand 15 minutes. In this way only smaller particles were obtained which permitted a measurement of their cataphoretic velocity to be made without the particles settling out of focus of the microscope. As mentioned before, the readings were taken one-fifth the distance from the bottom of the cell. The velocities of migration of the particles are expressed in μ per second per volt per centimeter. The readings were obtained within a temperature range of 26.5° to 28.5°C. Eucalyptus oil was not included in the general procedure as used by Taylor and Bull (18). Parallel experiments were run, however, which included the effect of eucalyptus oil in pure water and also in the presence of aluminum nitrate, silver nitrate, lead nitrate, and thorium nitrate on the cataphoretic velocity of galena and of quartz in the presence of aluminum nitrate. A series of experiments was conducted in which the oil was added to the suspension of the mineral in the electrolyte, and another series was investigated where the oil was added to a pure water suspension of the mineral and the electrolyte added afterwards. In no case was there any observable difference in the electrokinetic potential between the two series, nor was there any observable difference whether the eucalyptus oil was present or not.

[2] Kindly contributed by Dr. Gruner of the Department of Geology of the University of Minnesota.

RESULTS

The effect of potassium ethyl xanthate on the electrokinetic potential of galena and quartz was investigated. In the concentration normally used in flotation (1/10 lb. per ton of ore), there was no observable effect. In more concentrated solutions the negative potential is increased. In concentrations about one hundred times as large as that normally employed a peculiar phenomenon takes place. There is a flocculation of small particles (2μ in diameter) into single needles of approximate dimensions of $2\mu \times 2\mu \times 10\mu$. These needles have a negative electrokinetic potential almost twice that of the original small particles.

The cataphoretic velocity of all the minerals suspended in pure water may be summarized as given in table 1. It is interesting that the carbonates carry a positive charge. This is probably due to a hydrolysis of the carbonate in the following manner:

TABLE 1

Cataphoretic velocity of minerals suspended in pure water

MINERAL	VELOCITY	MINERAL	VELOCITY
	μ/sec./volt/cm.		*μ/sec./volt/cm.*
Sphalerite	−2.82	Galena	−2.34
Pyrite	−1 95	Galena exposed to air for 5 days	−2.36
Anglesite	0.0	PbO_2	+1.21
Cerussite	+3.13	$PbSO_4$	+1.82
Malachite	+0.63	PbO	+1 05
Rhodochrosite	+1.91		

$$PbCO_3 + H_2O \rightarrow PbHCO_3^+ + OH^-$$

The effect of the addition of electrolytes on the electrokinetic potential of galena is shown in figure 1 and their effects on quartz and sphalerite in figure 2.

DISCUSSION

It should be emphasized that though the endeavor was made to maintain the same condition in this study as used by Taylor and Bull (18) in their flotation experiments there were some differences, and these must always be kept in mind in interpreting the cataphoretic studies in terms of flotation. In the flotation experiments a 50-g. lot of galena was present in about the same amount of suspension as 0.57 g. in these experiments. There was undoubtedly some adsorption of electrolyte which will therefore alter concentrations and also, although purest galena obtainable was used in both cases, we cannot be sure we had exactly the same degree of purity.

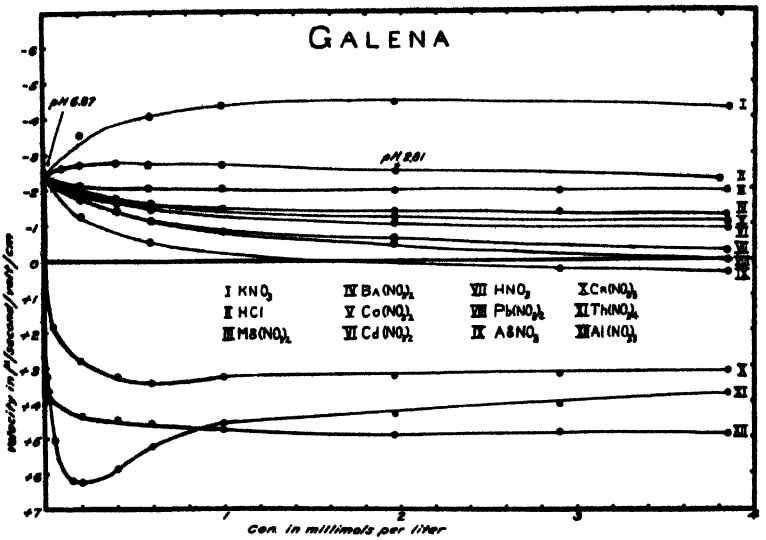

FIG. 1. SHOWING THE EFFECT OF ELECTROLYTES ON THE MOBILITY OF GALENA

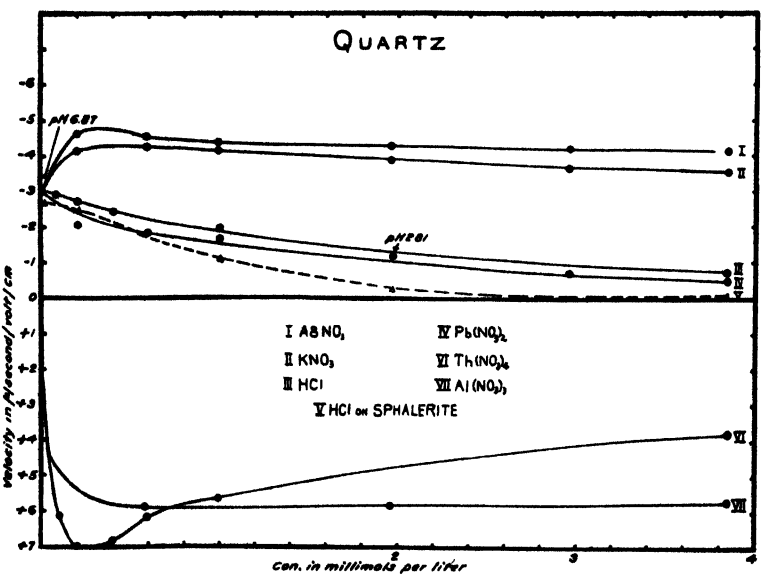

FIG. 2. SHOWING THE EFFECT OF ELECTROLYTES ON THE MOBILITY OF QUARTZ

However, in spite of these factors, the results do enable us to answer some earlier suggestions. For example, once an air bubble has become mineralized the charges of particles already attached may tend to keep other particles from attaching, owing to repulsion by like charges. If this

alone were the cause of the loss of galena in flotation in the presence of certain cations then figure 1 would indicate that galena with eucalyptus oil in pure water should float less readily than when the nitrates of Mg^{++}, Ba^{++}, CO^{++}, Cd^{++}, and Pb^{++} are present. Furthermore the floatability of galena in presence of silver nitrate should pass through a maximum at a certain concentration where the charge on the particle is zero. On the other hand, these salts all reduce the floatability of galena by eucalyptus oil (18). Figure 1 would also indicate that potassium nitrate might be as toxic as thorium nitrate.

We find that floatability of galena varies directly as the potential on the particles in the case of Ag^{+}, Pb^{++}, Cd^{++}, Co^{++}, Ba^{++} and Mg^{++}, and further that the order of the toxicity of the nitrates Ag > Pb > Cd > Co is exactly that of ability of the cations to reduce the electrokinetic potential on the galena. This would indicate that flotation is a matter of peptization rather than flocculation, and it may be interpreted that the larger surface of the peptized material offers greater opportunity for collecting agents to become adsorbed and build up a nonpolar coating. Later these coated particles are taken up by the air bubbles. This view harmonizes with certain statements in Gaudin's excellent book (12). "Far from considering general flocculation is necessary, it would seem as though reasonably good dispersion is desirable for successful flotation, because if it does not obtain, the opportunity to react with the reagents and to adhere to air bubbles is not fully presented to particles that occur within the floccules. The production of a dispersed pulp would then appear as the first requisite in a slimy pulp, and treatment with proper reagents to bring the selection of certain minerals should come next."

The inhibition of flotation by the nitrates of thorium, aluminum, and chromium may be due to formation of hydroxides which are more hydrophilic than the original sulfide.

It seems to be rather generally believed that galena surfaces oxidize to give a surface of lead sulfate (1, 8, 13). According to information supplied by Gaudin (12) this oxidation takes place rapidly. The effect of atmospheric oxidation of galena on the cataphoretic velocity was studied by determining the potential immediately on rapid grinding and then allowing the galena to remain exposed to air for five days. The loss in negative potential was not more than 5 per cent. Then the galena was heated to 300°C. in a stream of air for two hours and the negative potential had been reduced by 20 per cent. Pure anglesite ($PbSO_4$) exhibited no potential; pure cerussite ($PbCO_3$) gave a relatively large positive potential equivalent to a velocity of 3.1μ per second per volt per centimeter. Laboratory chemicals PbO, PbO_2, and $PbSO_4$, all exhibited positive potentials. Since the electrokinetic potential is a surface phenomenon, these experiments seem to indicate that the oxidation is by no means rapid.

It is interesting to note the effect of hydrochloric acid on the cataphoretic velocity of galena as contrasted with that of nitric acid. The increased potential with hydrochloric acid is possibly due to the tendency to adsorb chloride ions because lead chloride is more insoluble. It is also interesting that silver nitrate lowers the potential very much. This may be due to the large adsorption of the silver ion, since silver sulfide is very insoluble.

The previous results reported by Bull (3) on the electrostatic charge on galena using the Dorn effect have not been confirmed.

SUMMARY

1. Cataphoretic studies have been made on a number of pure minerals suspended in pure water. The study has been extended in the case of galena, quartz, and sphalerite to include several electrolytes at various concentrations.

2. Comparison of the data on surface charge of galena with our earlier work on flotation under similar conditions of added electrolytes shows that peptization rather than flocculation is a necessary requisite for good flotation, to be followed by the addition of suitable collecting agents.

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NEW BOOKS

Grenzflächen-Katalyse. By MARTIN KRÖGER. 22 × 15 cm.; viii + 387 pp. Leipzig: S. Hirzel, 1933. Price: 10.50 M.

This book consists of a series of papers dealing with measurements of various physical properties of finely divided solids in relation to catalysis and adsorption, and, as such, presents a valuable and very considerable body of experimental material due to the work of Professor Kröger and his collaborators.

The physical variants studied include changes in the electrical conductivity, in the dielectric constant, and in the magnetic properties of catalysts during reaction and adsorption. These certainly offer some indication of the condition of the catalyst during the process in question; and Professor Kröger is to be congratulated on the thoroughness with which the measurements have been carried out. At the same time, the correlation of catalyst composition with the reaction mechanism is frequently difficult. This is also true of the interpretation of the changes in the velocity and intensity of sound waves, which have been used in the investigation of the condition of gases during reactions in contact with finely divided solids.

Of special interest in connection with the energetics of catalysis is the section dealing with the limitation of the oxidative degradation of naphthalene. The function of catalysts such as vanadium pentoxide in inducing not merely a process of gross oxidation but also the effective stoppage of the oxidation at the phthalic anhydride stage is certainly of primary importance in the understanding of the general mechanism of all reactions of this type.

Probably the outstanding feature of the series of papers lies in the unusual nature of some of the methods of attack.

E. B. MAXTED.

Fundamentals of Fibre Structure. By W. T. ASTBURY. 15 × 22 cm.; ix + 187 pp. London: Oxford University Press (Humphrey Milford), 1933. Price: 8/6 net.

Mr. Astbury has here made available in book form a series of six university extension lectures which he gave to Yorkshire textile students early in 1932. The author is an acknowledged authority on the structure of fibres, particularly protein fibres of the animal body, such as hair and wool, and a wide range of readers will welcome this account. Reprinted lectures, while preserving the freshness of the spoken word, always suffer from the special nature of the audience for which they were prepared. In this case the reader may or may not welcome seventy-six pages on the nature of matter and radiation, the invisible fibres of the world of molecules, and an elementary account of how atoms make spatial patterns. The remaining three lectures deal in a vital way with the author's own researches and those of his colleagues. The general reader will feel that precision has been brought into a very difficult field of organic chemistry, and the specialist will marvel that so much precise information has been obtained from such fuzzy x-ray photographs. The crystallites of hair and wool are very minute and the remaining amorphous matter increases the difficulties of inpretation. Mr. Astbury shows how the extensibilities of hair and wool are due to the unfolding of the keratin chains and his facts are linked up in a novel way with the technical processes of the woolen industry. The book is appropriately introduced by Sir William Bragg and concludes with a useful bibliography.

J. T. RANDALL.

Pour Comprendre la Chimie Moderne. By E. CATTELAIN. 18 × 11 cm.; 254 pp. Paris: G. Doin & Cie., 1933. Price: 15 francs.

There are some who will condemn this book merely because the theory of atomic structure is introduced on p. 24, whereas no mention of a buret is made until p. 150. In a book of this type addressed to the layman there is, however, something to be said for using this theory as a framework into which the facts of chemistry may be fitted, in spite of the obvious risk that the stability of the whole structure may be thought to depend on this framework. Granting this, certain features of the arrangement of the subject matter may prove useful to teachers who have to "explain" modern chemistry to those who have not had an experimental initiation into the science. On the other hand, the book should not be put into the hands of the novice who might aspire to become a serious student of Chemistry. Apart from acquiring strange ideas about the scope of organic chemistry (p. 17) and regarding the structure of an "unionised molecule" of sodium chloride (p. 236), he would be completely confused in his attempt to understand the explanation of how the volumes of gases participating in a reaction are shown by the chemical equation (p. 73), since the author habitually writes the formulas of hydrogen, oxygen and nitrogen as if their molecules were monatomic.

H. J. T. ELLINGHAM.

Theorie der Oberlächenerscheinungen. Edited by A. R. RABINOWITSCH, N. A. BACH and A. G. PASSYNSKI. Charkow, Russia: Technischer Staatsverlag, 1933.

During September 20–24, 1932, a symposium on "The Properties of Surfaces" was held at Moscow, Russia, under the auspices of the "Assoziation Physikalisch-Chemischer Forschungs-Institute im Karpow-Institut für physikalische Chemie, Moskau." The papers presented at this symposium appear in Band 4, Heft 2, pp. 139–432 (1933), of the "Physikalische Zeitschrift der Sowjetunion." All papers appear in either German or English. This Symposium may be regarded as more or less analogous to the Colloid Symposiums which have been held annually for the past ten years in the United States. The following twenty-three papers, all dealing with problems of surface chemistry or surface physics, are included in the monograph:

M. Polanyi. Adsorption und Kapillarkondensation.

M. Dubinin. Kapillarkondensation von Dämpfen an porösen Sorbenten.

M. O. Charmadarjan und W. K. Markow. Einfluss der Reaktion des Mediums im Moment der Koagulation auf die Struktur des Silikagels. I.

F. P. Bowden. On the Range of Surface Forces.

R. Burstein, P. Lewin und S. Petrow. Aktivierte Adsorption von Gasen an Kohle.

P. I. Lukirsky. Über die Austrittsarbeit der Elektronen und die photoelektrischen Eigenschaften der Metalle.

A. Frumkin. Ionenadsorption an Metallen und Kohle.

E. Lange. Über die Natur der Quecksilbertropfelektrode.

B. P. Nikolski. Die Eigenschaften der Doppelschicht und die Austauschadsorption von Ionen an nichtmetallischen Oberflächen.

L. Lepin. Die Oberflächenoxyde der Kohle und die Adsorption von Elektrolyten.

H. R. Kruyt. Kapillar-elektrische Untersuchungen an Silberhalogeniden.

A. J. Rabinowitsch. Adsorption der Elektrolyte und ζ-Potential.

L. W. Janssen. Der Aufbau der elektrischen Doppelschicht.

M. O. Charmadarjan und B. I. Perwuschin. Über einige Erscheinungen bei der Bewegung einer der Elektroden im Elektrolyten und über das elektrokinetische Potential.

F. P. Bowden and A. Dummett. The Influence of the Underlying Surface on the Cataphoretic Mobility of Adsorbed Proteins.
M. Volmer. Überspannung.
R. W. Gurney. Quantum Mechanics and Overpotential.
P. A. Rehbinder und N. Kalinowskaja. Abnahme der Grenzflächenenergie und Zunahme der Dispergierbarkeit fester Körper bei Bildung einer Adsorptionsschicht.
W. P. Berdennikow. Messung der Oberflächenspannung von festen Körpern.
D. L. Talmud. Mechanische Eigenschaften der Adsorptionsschichten und Stabilität der Schäume und Emulsionen.
B. V. Deriagin. Mechanical Properties of Thin Layers of Liquids.

Space will not permit an evaluation of the individual contributions in this review. Suffice it to say that many of the papers are of the utmost importance and should be carefully read by those interested in the properties of surfaces. The volume can be secured through the American agents, G. E. Stechert and Company, 31 E. 10th St., New York City.

ROSS AIKEN GORTNER.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 54: Wolfram. 25 × 17.5 cm.; xi + 397 pp. Berlin: Verlag Chemie, 1933. Price: 64 M. Subscription price: 56 M.

This volume includes the sources and ores of tungsten, the preparation of the metal, including technical processes and the production of wire for the lamp industry, physical properties, chemical properties, analysis, alloys, and compounds. Among the latter the salts of tungstic acid are fully dealt with, together with the question of the basicity of the tungstic acids. The complex molybdic acids, such as borotungstic, silicotungstic, and phosphotungstic acids, are included. The volume gives a modern and very complete account of the chemistry of tungsten and is of the same high standard as its predecessors. In view of the importance of tungsten in modern industry, such a monograph is very welcome.

J. R. PARTINGTON.

Recent Advances in Physical Chemistry. By SAMUEL GLASSTONE. Second edition. 14 × 21 cm.; viii + 498 pp. London: J. and A. Churchill, 1933. Price: 15 shillings.

This well-planned and well-written summary of recent advances in physical chemistry has won for itself a place in the library of most advanced students of the subject, and the appearance of a second edition will be heartily welcomed. No change has been made in the general plan of the book, except that the chapter on solubility, perhaps the least necessary or important chapter in the former edition, has been omitted; and the space which has thus been made available has been more than used up in expansions of the remaining chapters. The groundwork of the book remains largely unchanged, although here and there certain paragraphs have been rewritten or modified, and the value of the present edition as compared with its predecessor lies in the new matter which has been inserted. The new subjects discussed include: wave mechanics and its applications to problems of valency and the calculation of energy of activation; nuclear disintegration and the discovery of the neutron and the positive electron; the influence of free and restricted rotation on dipole moments; molecular beams and their uses; potential energy curves; atomic reactions; the kinetics of photochemical reactions; activated and discontinuous

adsorption; surface potentials; the mobility of surface molecules. In the case of a number of these subjects many will, perhaps, feel that the treatment is rather slight and inadequate, but even if this may be so, the discussion of the various topics, all of considerable interest at the present time, will direct the attention of the serious student to the paths along which the subject is advancing and will help him to take up the fuller study of one or more of the subjects discussed. More than this can scarcely be demanded of such a book as the one under review.

A. FINDLAY.

Die Lösungsgleichgewichte der Systeme der Salz ozeanischer Salzablagerung. By J. D'ANS. Quarto, 254 pp.; accompanied by 31 tables of graphs and diagrams, which are bound separately. Kali-Forschungs-Anstalt, Berlin. Verlagsgesellschaft für Ackerbau, M.B.H., Berlin S.W. 11, Dessauer Strasse.

The writer of this monograph, who worked in the laboratory of van't Hoff on this subject, has here revised and recompiled all of the information relating to it now available. It forms a complete summary of the facts known regarding the equilibria which exist between water and salts yielding chloride, sulfate, sodium, potassium, magnesium, and calcium ions, in either their simplest or most complex mixtures. In part I, one finds forty-seven pages devoted to a clear and systematic discussion of solubility determinations, methods of ascertaining the composition of the solid phases left after such determinations, and methods of fixing the constants which define invariant points; also the results of the application of the phase rule to the study of such data and discussion of the graphical methods of representing such systems. There are one hundred and eighty-eight pages devoted to the discussion of the forty-six salt systems, in which all of the data relating to combinations of water and from two to all six of the ions named, have been compiled and submitted to critical analysis. One is surprised at the large amount of such data which has accumulated since the last summary by van't Hoff.

The composition of solutions has been recalculated, where necessary, and tabulated in terms of moles or double moles per 1000 moles of water, and in many cases in grams per 100 grams of water also. These data have been plotted on coördinate paper on a scale of 2.5 moles or 2.5 degrees per centimeter, the most probable course of the corresponding graphs drawn, and the whole reduced by photographic reproduction to a series of graphs and diagrams on which one centimeter represents 5 moles or 5 degrees. It is possible therefore, with the use of a lens, to read off compositions to 0.1 mole and temperatures to 0.1 degree. These graphs and diagrams make up most of the material reproduced on the thirty-one plates of part II. The volume clearly represents the results of an enormous amount of work and gives evidence of having been thoughtfully and carefully compiled and edited.

W. C. BLASDALE.

STUDIES IN AUTO-OXIDATION REACTIONS. VII

THE DATIVE OR COÖRDINATION PEROXIDE THEORY OF AUTO-OXIDATION[1]

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In a recent paper published in This Journal, Stephens (38) has advanced some arguments against the dative peroxide theory of auto-oxidation (27a, 27b) and concluded somewhat dogmatically that the initial stages postulated by this theory have no justification. It is the purpose of this paper to point out that Stephens' arguments are not entirely justifiable and in several cases are somewhat inconsistent with facts, and to bring forth additional evidence in favor of the dative peroxide theory.

When this theory was first enunciated some years ago, the present author made a careful investigation of the chemical behavior of numerous substances which are capable of auto-oxidation. This study revealed the fact that all substances capable of combining with molecular oxygen are known to be unsaturated towards reagents other than molecular oxygen. The apparent exception of saturated hydrocarbons is easily accounted for by the assumption originally made by Mardles (23) and independently by the present author (reference 27b, p. 347) that combination of molecular oxygen with saturated hydrocarbons occurs either through free radicals (highly unsaturated towards other reagents) or through the exposed electrons resulting from the activation of hydrocarbon molecules prior to their decomposition. Hydrocarbons, especially of the hexaphenylethane type, are known to split very readily into free radicals which add molecular oxygen with considerable avidity.

The presence of unsaturation in auto-oxidant molecules is confined entirely to certain atomic nuclei in each molecule known to possess loosely bound molecular valence electrons which can be easily donated to other nuclei by sharing. That these electrons are loosely bound in certain nuclei of polyatomic molecules has been recently amply demonstrated by Mulliken (29). This author gives the electronic structures of NH_3 and H_2O as $1s^2\ 2s^2\ 2p\ (\pi)^4 2p(\sigma)^2$ and $1s^2\ 2s^2\ 2pa^2 2pb^2 2pc^2$, respectively, and states that "the two $2p\ (\sigma)$ electrons in NH_3 avoid the region of the H nuclei, and as a

[1] Contribution No. 94 from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology.

result are relatively loosely bound and reduce the energy of formation of the molecule." "Direct evidence of these electrons in NH_3 is given by the low ionization potential of this molecule, which is 11.1 volts. Many features of the chemical behavior of NH_3, e.g., the formation of NH_4^+, $H_3N \cdot BCl_3$, $Cu^{++}(NH_3)_4$, etc., are reasonably interpreted as conditioned by the stabilization of the two loosely bound $2p(\sigma)$ electrons of NH_3 under the influence of an additional nucleus." The ionization of a $2p(\pi)$ electron of NH_3 would take, according to Mulliken, 15 volts, while that of a $2s$ electron, 25 volts.

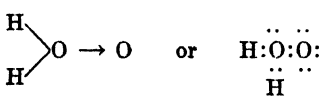
Although NH_3 reacts with oxygen only at relatively high temperatures, several of its derivatives are known to auto-oxidize quite readily. Sodamide, for example, adds molecular oxygen to form sodium amidoperoxide, $NaH_2N \cdot O_2$ (35). Several aryl amines, hydrazones, etc., can be isolated only in the form of their salts in which the $2p(\sigma)$ electrons are stabilized (reference 27a, p. 1211). Furthermore, the instability of free radicals, like the methyl radical, is, according to Mulliken (29), due to the presence in the radical of a $2p(\sigma)$ electron.

It has already been suggested elsewhere (reference 27a, p. 1211) that the tendency to auto-oxidize of the hydrides and aryl derivatives of the elements of the fifth group of the periodic table increases as the "effective nuclear charge" of the central elements increases. If the auto-oxidation of these substances proceeds through a preliminary addition of molecular oxygen to the unshared pair of electrons present in each molecule, then there ought to exist a relationship between the tendency of these substances to auto-oxidize and their ionization potentials. That such a relationship actually exists not only with the hydrides of the elements of the fifth group, but also with those of the sixth and seventh groups, has been recently pointed out by the author (28). It has been shown that as we pass down in each group from the lightest to the heaviest element, there is a regular decrease in the ionization potentials of the hydrides, which means an increase of looseness of the molecular valence electrons. With an increase of looseness of these electrons, there ought to be a corresponding increase in the tendency to auto-oxidize. This is made obvious when we compare the first ionization potentials of the alkali and alkaline earth metals with their tendency to oxidize. It has been found that with a decrease in the ionization potentials there is a corresponding increase in the tendency to auto-oxidize.

These considerations should not be confined to the inorganic substances, since the principles of oxidation and reduction apply equally well to organic substances. When molecular oxygen combines with an organic substance, the latter contributes two electrons to it, and the ease with which these electrons are contributed usually determines the reducing power or the oxidizability of the substance. Furthermore, the ease with which molecu-

lar oxygen takes up these electrons to form the peroxide group may also depend upon its electron affinity, or the energy required to remove two electrons from the peroxide ion, O_2^{--}. Unfortunately there are no data available at present which will enable us to estimate this electron affinity. Noyes and Beckman (30) have calculated the electron affinity of atomic oxygen for the first electron and found it to be 4.6 volts. Whether that of the molecular oxygen for two electrons is of the same order of magnitude is not known. As an oxygen molecule approaches an easily oxidizable substance, it is easily conceivable that it may attract electrons from the latter with a force equal to its electron affinity, or, in other words, it may reduce the ionization potential of the auto-oxidizable substance.

Some evidence in favor of the electronic structure of the reacting oxygen molecule originally proposed by the author, is to be found in the structure of hydrogen peroxide recently proposed by Maas and his students (5, 8, 21). From a study of the dielectric constant, molecular refractive power, and the parachor of hydrogen peroxide, these investigators proposed the unsymmetrical structure,



which also agrees with the ease with which hydrogen peroxide loses an oxygen atom to form water. This structure is probably in equilibrium with the symmetrical structure. Since hydrogen peroxide is known to form by the addition of hydrogen to molecular oxygen, its unsymmetrical structure provides evidence for our electronic structure of the reacting oxygen molecule. However, as has been emphasized elsewhere by the author (reference 27b, p. 300), the "odd" electronic structure proposed by Lewis should not be excluded in auto-oxidation reactions.

Although some of the molecular valence electrons, present in many of the auto-oxidant molecules, are apparently paired, it is not certain that this condition holds when these molecules are activated or excited. Moreover, several of the auto-oxidants, such as nitric oxide, the alkali metals, ferrous and chromous compounds, and free organic radicals, in general, are definitely known to possess unpaired valence electrons through which they interact with other molecules.

Auto-oxidation reactions are strongly exothermic and in numerous cases are chemiluminescent. Bäckström has clearly demonstrated that chemiluminescent reactions reveal the presence in the reaction system of molecules of exactly the same kind as are produced by the absorption of light of the same or higher frequency as the emitted light. Furthermore, the energy transferred during auto-oxidation reactions to the reactant molecules, presumably by collisions of the second kind, excites these molecules

into those quantum states which are responsible for their ultra-violet spectra. That this energy is of chemical origin can be easily shown by the fact that the heat of reaction is usually greater than the energy of excitation which corresponds to the wave length of the emitted light.

In the case of benzaldehyde, for example, Bäckström has shown that the region of strong light absorption is approximately 3800 A.U., corresponding to an energy of excitation of 75 kg-cal. The heat of auto-oxidation of this substance is 140 kg-cal., which is more than sufficient to cause the excitation of benzaldehyde molecules. Another notable example is the thermal decomposition of ozone, which shows a heat of reaction of 69 kg-cal. whereas the longest wave length in its absorption spectrum corresponds to an energy of excitation of only 47 kg-cal.

If the energy of excitation in auto-oxidation reactions were entirely of vibrational origin, as Stephens seems to assert, one would expect infra-red light to have an accelerating effect in these reactions. As far as the present author is aware, there is no evidence that this is the case. On the contrary, the decomposition of hydrogen peroxide which follows a chain mechanism is totally unaffected by the absorbed infra-red light, while it is greatly accelerated by ultra-violet light (18).

Moreover, there exists a strong parallelism between the photochemical and the thermal auto-oxidations. Both have a chain mechanism; both are susceptible to the influence of negative and positive catalysts. Another parallelism closely related to this one is that between the effects of peroxides and ultra-violet light on certain chemical reactions. Both are known to accelerate auto-oxidation reactions, to induce polymerization of unsaturated substances and to affect the photographic plate. Furthermore, the recent observations of Kharasch and his students (16, 17) and of Smith (36) seem to indicate clearly that in the presence of oxygen or peroxides the olefinic bond is polarized in such a way as to influence the direction of the addition of hydrogen bromide to it. Other additional reactions to the double bond cannot be easily understood unless we assume with Lowry (22) and with Carothers (7) that the reacting molecules are polar or electrovalent, in which two of the electrons have been displaced towards one or the other carbon atom. In fact, it is because of this displacement of the electrons that we are justified in speaking of these substances as unsaturated molecules (20). The fact that the electric moment of ethylene and of other unsaturated substances is found to be zero does not disprove the assumption that the reacting unsaturated molecules are polar. This has been clearly stated recently by Smyth (37).

Finally, the foregoing considerations lead to the unescapable conclusion that the mechanism of the formation of excited molecules is the same in the dark or in photochemical auto-oxidation reactions, and that these ex-

cited molecules are produced by the simultaneous supply of vibrational and electronic energy.

AUTO-OXIDATION OF HYDROCARBONS

The fact that saturated hydrocarbons auto-oxidize is not at variance with the general theory proposed by the present author, as Stephens seems to insist, since the theory assumes the addition of molecular oxygen to molecular valence electrons which are exposed either as the result of excitation of the hydrocarbon molecule or of its dissociation to free radicals. Whether the final peroxide is an alkyl hydroperoxide or a dialkyl peroxide depends entirely upon the hydrocarbon in question and the relative strengths of the bonds concerned. This point has been more fully discussed by the author elsewhere.

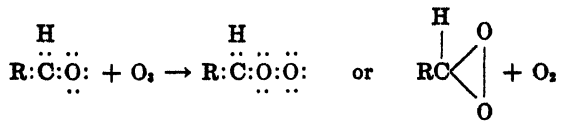
With regard to the auto-oxidation of unsaturated hydrocarbons, there is a displacement of electrons prior to the addition of oxygen, a condition which is fulfilled only by the theory of the present author. The effective strength of the bond broken in the auto-oxidation of an ethylenic substance may be taken as the difference of the strengths of the double and the single bonds. Taking the strength of the C—C bond as 80 kg-cal. (33), and that of the C=C bond as 123 kg-cal. (39), this difference comes out as 43 kg-cal. which is not very far off from the experimentally obtained activation energy for the oxidation of ethylene, namely, 35 to 43 kg-cal. (40). This indicates that in the activated ethylene molecule the double bond is probably broken with subsequent displacement of the electrons to form the polar double bond discussed in the previous section.

AUTO-OXIDATION OF ALDEHYDES, ETC.

Pure aldehydes are not known to dehydrogenate easily, as Stephens claims; in fact, we know of no case in which aldehydes dehydrogenate easily, say, to form diketones even in the presence of dehydrogenating catalysts. Furthermore, Eyring (10) has shown recently that in the case of acetaldehyde, for example, the C—H bond is stronger than the C—C bond. Such arguments, therefore, as those proposed by Stephens are entirely irrelevant to the auto-oxidation of aldehydes in which the seat of unsaturation lies in the carbonyl group. Both Wolf (41) and Smyth (37) have concluded that the electric moment of aldehydes is inherent in the carbonyl group with the oxygen being the negative end of the dipole.

Hydrogen peroxide and ozone are stronger oxidizing agents than molecular oxygen, yet in neither case does the hydrogen of the alpha carbon atom of aldehydes oxidize easily to a hydroxyl group. In the case of hydrogen peroxide stable α-hydroxy peroxides and hydroperoxides are formed (34). Ozone, which is known to add on to unsaturated groups very

much in the same manner as molecular oxygen, forms alkyledine peroxides with aldehydes (13, 12, 11). These peroxides either polymerize or, when warmed up, go over to their isomeric acids.



In the case of the auto-oxidation of aldehydes the very recent work of Bodenstein (4), of Bäckström and Beatty (2) and of Kohler and Nygaard (19) confirmed the conclusion of earlier investigators that an active moloxide is first formed which subsequently rearranges to the peracid. Bäckström and Beatty state definitely that the direct formation of a peracid or an activated form of it in one step fails to account for their experimental results; accordingly they were forced to assume the existence of an intermediate moloxide originally proposed by Bach. These and various other considerations confirm our earlier view in regard to the mechanism of the auto-oxidation of these substances.

A similar view has been adopted in the case of the addition of oxygen to the ketones and thioketones. That the double bond in thioketones and thioaldehydes is virtually broken under ordinary conditions is shown by the fact that the aliphatic thioketones and thioaldehydes are known to exist only in their dimeric or trimeric modifications (3). This conclusion is strengthened by the high electric moment recently reported for some of these substances by Hunter and Partington (14). Contrary to the assumption of Stephens, no alkyledine peroxides are known to form in the case of the auto-oxidation of thioketones.

With regard to the mechanism of the auto-oxidation of ethers, there exists ample chemical evidence on oxonium compounds (31, 32, 24) which supports the correctness of our original conclusion that an unstable oxonium or dative peroxide is initially formed.

Finally, the auto-oxidation of triethylphosphine and related substances proceeds, as has already been shown elsewhere, through the initial formation of dative or triethylphosphonium peroxide. Stephens disagreed with this view and proposed an initial peroxide in which the phosphorus atom still retains its original valence of three. This is contrary to our knowledge of the chemical behavior of this class of compounds towards oxidizing agents. The main stable product of this reaction is triethylphosphonium oxide, while secondary products formed by the interaction of this oxide with the peroxide have also been isolated (9, 15, 25). If the peroxide proposed by Stephens were the initial product, one would expect it to hydrolyze in presence of water to yield ethyl hydroperoxide. Actually, no such product is known to form. That the oxide is the main final product is clearly

shown by the auto-oxidation of triethoxyphosphine, $(C_2H_5O)_3P$, to form first the peroxide and then triethoxyphosphonium oxide, $(C_2H_5O)_3PO$ (42). Another example of this type is the auto-oxidation of phosphorus trichloride, which yields phosphorus oxycloride (26).

Trimethylarsine and other alkylarsines are also auto-oxidized to yield through the intermediate peroxides alkylarsonium oxides (6).

SUMMARY

1. Additional evidence has been given in favor of the dative peroxide theory of auto-oxidation originally proposed by the author.

2. It has been shown that the recent criticism of this theory is entirely unjustifiable.

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STUDIES IN AUTO-OXIDATION. IV

THE MECHANISM OF ADDITION OF OXYGEN

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The paper immediately preceding this one (6) attempts to defend against recent criticism (14) and to substantiate further the dative peroxide theory of auto-oxidation (5). It also attempts to refute the arguments advanced by the writer (14) in favor of his own viewpoint. In view of the fact that neither the defense of the former theory nor the criticism of the latter is convincing, it becomes necessary to extend the earlier criticisms of the dative peroxide theory to include the most recent arguments of its proponent and to add to the justification of the opposing theory of the writer.

MOLECULAR VALENCE ELECTRONS

The writer has already conceded (15) that molecules such as those considered by Mulliken (9) and Birge (1) contain electrons which may be properly considered as valence electrons. It may be added that odd molecules and free radicals undoubtedly belong to this group. However, it cannot be admitted that such a capacity can be indiscriminately attributed to all unshared electrons in molecules.

In view of the fact that the foregoing article by Milas directs attention particularly to the hydrides of the elements of groups V, VI and VII in the periodic table it will be convenient to consider them here also. Taking ammonia as an example, it is assumed that its two unshared electrons are capable of functioning as valence electrons. This is true, however, only in a very restricted sense, as it is only[1] in cases involving the attachment of a proton or positive ion to the ammonia molecule, that the unshared pair of electrons in the latter plays a rôle similar to that of valence electrons. In other words, the addition reactions of ammonia are highly specific and depend upon what is called, in the absence of a more general term, the proton affinity of the molecule. In the typical case of the addition of HCl, the resultant ammonium ion acquires a positive electrovalence of one, which is merely the valence of its fourth proton,

[1] The possibility of exceptions in the addition compounds of ammonia with the hydrides and halides of boron is, in the meantime, disregarded, owing to lack of knowledge of the structure of these erratically varied substances.

the valence of the nitrogen thus remaining unchanged. On the other hand, addition reactions of such molecules as CO, CO^+, BeF^+ etc., which admittedly contain true valence electrons, will necessarily involve valence changes. It will be obvious, then, that direct analogy between ammonia and these molecules is of extremely doubtful validity.

Following further the arguments of Milas, it is clearly implied that the formation of -onium compounds is due to "unsaturation" in the donor molecules. It has just been indicated, however, that the formation of these salts is a highly specific reaction involving the addition of a positive ion from the addendum. Typical unsaturated compounds such as ethylene and its derivatives do not show this specificity nor do their hydrohalides in any case exhibit more than a very feeble approach to the properties which we associate with salts. Consequently, the addition reactions of the ethylenes cannot be compared with those of compounds which form -onium salts. If the term "unsaturation" is used at all in the latter cases it ought to imply a special connotation. In the opinion of the writer the property in question ought to be called proton affinity and sharply distinguished from unsaturation. To illustrate the necessity for this distinction may we consider further the behavior of the group V hydrides and their derivatives.

It is common knowledge that the proton affinity of these hydrides decreases regularly with increasing atomic weight of the central element. When we reach phosphine the capacity of forming a base with water has practically disappeared and later the capacity of salt formation vanishes. A similar trend is evident in the alkyl and aryl derivatives.

Now, if we examine the tendency to auto-oxidize we find precisely the opposite trend, ammonia and the amines being the least susceptible to molecular oxygen and the activity toward oxygen increasing as we pass down the group. Trimethylstibine catches fire in air at ordinary temperature, while trimethylamine is relatively difficult to oxidize.

Furthermore, to make the argument more conclusive, the proton affinity of nitrogen increases regularly as the hydrogen atoms in ammonia are replaced successively by alkyl groups, as evidenced by the increasing strength of the corresponding bases. On the other hand, replacement by aryl groups is paralleled by a decrease in proton affinity.

Once more we find that the tendency to auto-oxidize is exactly opposite in trend, as the aryl amines are very sensitive and the alkyl amines relatively indifferent to oxygen at ordinary temperatures. The inevitable conclusion is that the auto-oxidation of the group V hydrides is not related to their proton affinity. It seems logical to conclude further that proton affinity is not related to unsaturation, because decreasing unsaturation ought to involve a decrease in the tendency to auto-oxidize. It will be evident that such arguments as those above might be extended to include

other compounds which form -onium salts. These would include alcohols, ethers and aldehydes, and their sulfur analogues—in brief, the majority of the compounds used to illustrate the applicability of the dative peroxide theory.

It has just been pointed out that the tendency of the hydrides of group V to auto-oxidize is not related to proton affinity or to unsaturation. It is very obviously parallel to the thermal stability of the X—H bond and the writer feels justified in adhering to the viewpoint expressed earlier, that the point of attack in these hydrides and their organic derivatives is a vibrationally activated X—H or X—C bond. The hydrides of groups VI and VII are considered similarly, as are also those of group IV.

IONIZATION POTENTIAL AND AUTO-OXIDATION

In the preceding article by Milas it is pointed out that there exists a parallelism between the ionization potentials of the hydrides of groups V, VI, and VII and their tendency to auto-oxidize. This is compared to a similar parallelism in the alkali and alkaline earth metals.

TABLE 1

Ionization potentials

ELEMENTS	IONIZATION POTENTIAL*	HYDRIDES	IONIZATION POTENTIAL*
	volts		*volts*
Cl_2	13 2	HCl	13 8
Br_2	12.8	HBr	13.2
I_2	10 0	HI	12 8

* From Landolt-Börnstein Tabellen E. 384.

In the latter case the parallelism unquestionably involves a relationship, as the peroxides of the active metals are salts and their formation, therefore, involves an actual transfer of electrons. In the former case, however, there seems every indication that this is not so. The electron affinity is undoubtedly smaller for molecular than for atomic oxygen, which, as Milas has pointed out, has been estimated at 4.6 volts (10). Therefore if we consider, for example, the oxidation of ammonia, with an ionization potential of 11.1 volts, the activation energy necessary to accomplish the transfer of two electrons to the oxygen molecule could hardly be less than 7 volts. As this is an impossibly high value, the natural inference is that the reaction proceeds by some other mechanism, involving an activation energy more in accord with experience.

If it were justifiable to assume with Milas that auto-oxidation proceeds invariably through donation of a pair of electrons to the oxygen molecule and if, as is implied in the foregoing paper, the ease of this donation is determined by the ionization potential of the donor molecule, one would

expect, for example, that the halogens in molecular form would be more readily auto-oxidized than their corresponding hydrides. The ionization potentials in question appear in table 1. It might further be expected that xenon, with an ionization potential of 11.5 volts, would be more readily auto-oxidized than any of the halogen hydrides.

POLAR STRUCTURE AND AUTO-OXIDATION

The application of the dative peroxide theory requires the assumption of polar structures for ethylene and its derivatives and for the oxygen molecule, to which the writer has objected (16). In this case it is unnecessary to argue the fundamental question of the possibility of such structures, but merely to consider the application employed by Milas. In the preceding paper it is concluded that, in the activation of ethylene, prior to oxidation, "the double bond is probably broken, with subsequent displacement of the electrons to form the polar double bond." May we now outline the conditions specified by the dative peroxide theory as necessary for the auto-oxidation of ethylene: (1) activation energy must be supplied; (2) the activated molecule must assume the unsymmetrical electronic structure; (3) the polar molecule will react only with a polar molecule of oxygen.

With respect to condition 2, our general knowledge of the reluctance of carbon to participate in the electrovalent type of linkage seems to preclude any possibility of a definite state with any permanence having the extreme separation of charges of the polar molecule (4). It is to be admitted, of course, that there will be a certain small probability of such an electronic configuration being found instantaneously, but there seems no possible reason for such an arrangement having any stability. Therefore, only a very small fraction of the already activated molecules of ethylene would be instantaneously in a position to react with oxygen. This fact alone ought to be sufficient to cast some doubt on the validity of condition 2, but when there is further superimposed the restriction that only the polar form of oxygen can react with the very small fraction of activated ethylene molecules which happen to be in the polar configuration, the writer feels that this interpretation reduces itself to an absurdity. The absence of electric moment in oxygen, of course, limits the maximum possible concentration of polar molecules to a very small one.

ACTIVATION IN LOW-TEMPERATURE THERMAL REACTIONS

It has been pointed out by the writer (17) and elaborated upon by Milas (8) that thermal and photochemical auto-oxidations proceed through the same initial stage. It is reasonable, therefore, to assume that a similar energy of activation is required in each case. In low temperature dark reactions there is no apparent source of energy for electronic activation;

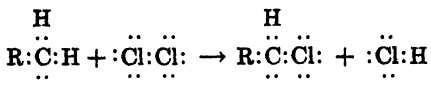
therefore the writer concluded that, as vibrational activation alone was possible in such cases, it must also account for photochemical oxidations. Milas attempts to discredit this viewpoint by pointing out the fact that the heat of oxidation, which may be transferred during the propagation of chains, is more than sufficient to supply energy of activation. This is quite true but irrelevant, as this author has apparently failed to realize that chains cannot be propagated before they are initiated. It is the initiation of chains that is the problem in thermal reactions. In the case of benzaldehyde, if we accept for the moment Milas' inference that its energy of activation is 75 kg-cal. and if we rely upon the Maxwell-Boltzmann distribution of energy for the initiation of chains, we find, at room temperature, approximately 1 molecule in 10^{32} moles with the necessary energy. Actually, however, the situation may not be as bad as this, in view of the fact that there is some evidence (2, 3, 11, 18) indicating that chains may be initiated at the walls. Even if this is invariably true, it is difficult to conceive of a surface activation involving electronic excitation, although something akin to vibrational "stretching" is not difficult to picture. Now, if chains can be initiated without the intervention of electronic excitation, they ought to be capable of propagation through the agency of bonds which possess only vibrational energy. The writer, of course, does not intend to fly in the face of all the evidence against the so-called radiation hypothesis by assuming that infra-red radiation ought to be effective in such reactions. The decomposition of hydrogen peroxide, cited by Milas (7), is simply one of many cases in which radiation corresponding to, or in excess of, the known energy of activation is ineffective. It would be out of place to introduce here a discussion of this apparent anomaly.

In the above arguments the writer has attempted to confine himself to essentials in the conflict between his own viewpoint and that of the dative peroxide theory. A detailed discussion of all the minor points brought forward in the preceding paper would require an unjustifiably large amount of space; therefore such points must be left to the judgment of the reader. In conclusion, however, it seems desirable to expand slightly and, in one instance, to modify the viewpoint expressed earlier in the paper on "The Initial Act in Auto-oxidation" (14).

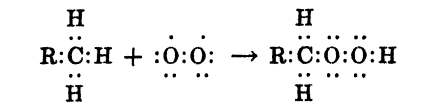
ADDITION OF OXYGEN TO A SINGLE BOND

The writer's interpretation of the auto-oxidation of the group V hydrides and their alkyl derivatives and of ethers, aldehydes, saturated hydrocarbons, etc., in which oxygen is represented as adding to a single bond, apparently does violence to the traditions of organic chemistry. According to these traditions addition reactions are characteristic of unsaturation, exhibited by multiple bonds or unpaired valence electrons. In order to

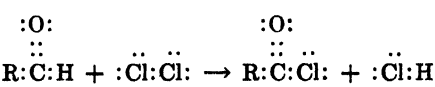
reconcile this apparent conflict an analogy will be helpful. If we consider the action of, say, chlorine upon a saturated hydrocarbon,



the sharing of pairs of electrons between chlorine and carbon and hydrogen, respectively, necessarily involves splitting of the chlorine molecule. In the parallel reaction of molecular oxygen, however, the two odd electrons of the latter may be shared without separation of the oxygen atoms.



From the same point of view the action of oxygen on an aldehyde may be compared to the corresponding action of chlorine, which yields acid chlorides



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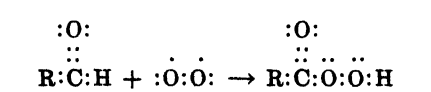
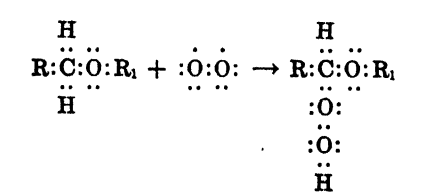


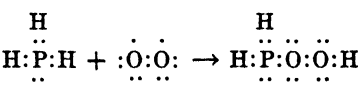
In the case of ethers the writer originally proposed the insertion of an oxygen molecule between the ether oxygen and one of the alkyl groups (17), but it now seems more probable that a C—H bond alpha to the oxygen is the point of attack.



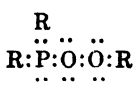
The reason for this modification is based upon the known predilection of oxygen for the α carbon atom (13), which is parallel to the behavior of halogens (12). Chlorination of ethyl ether is known to produce the compound $CH_3CHClOCH_2CH_3$ as the primary product. In this latter case,

as well as in the case of saturated hydrocarbons, cognizance is taken of the fact that thermal stability and reactivity toward a given reagent are not necessarily reciprocals of each other. If they were, we should expect halogenation of hydrocarbons to rupture a C—C linkage in preference to C—H, owing to the lower energy of the former bond. Similarly, ethers would be expected to split adjacent to the ether oxygen on halogenation.

To consider, finally, the hydrides of group V and their derivatives, it is known that chlorination of NH_3 yields NCl_3. Phosphine yields PCl_5, which probably is the inevitable addition product of chlorine with the primary PCl_3. Furthermore, there is evidence that intermediate compounds of the general formulas XH_2Cl and $XHCl_2$ are formed in the chlorination of NH_3, PH_3, and AsH_3 (19). These substitutions by chlorine may then be regarded as strictly comparable to those of the hydrocarbons. Now, if we carry further our analogy between chlorine and oxygen we should represent the first stage in the oxidation of, say, phosphine as follows:



In this instance we have no evidence of such an intermediate, but in the case of triethylphosphine, as has been pointed out before, the formation of a diethyl phosphinic ester is strongly suggestive of the isomeric antecedent,



It will be seen from the above considerations that the reactions of molecular oxygen may be placed in two categories, comparable to the addition and substitution reactions of the halogens. In both cases, however, the result is addition of oxygen; therefore unsaturation is not a necessary condition for such additions. On the contrary, the majority of additions of oxygen must be thought of as totally unrelated to unsaturation in the molecule to which the oxygen adds.

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ON THE RELATIONSHIP OF THE DISPERSION OF GOLD SOL TO THE INTENSITY OF REDUCTION AS INFLUENCED BY pH, AND A ONE-WAY EFFECT PRODUCED IN GOLD CHLORIDE BY CHANGES OF pH THROUGH CERTAIN RANGES

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That the production of gold sol is a procedure fraught with much uncertainty is admitted both by clinical pathologists, who are faced with the problem of production of colloidal gold for the Lange test, and by colloidal chemists. In a review of the many methods advanced for making gold sol, in which a great diversity of minutiae both as to technic and formulas are stressed, it was difficult to extract any generalizations that might lead to control of the process. The frequent inability of one laboratory to repeat the happy results of another would seem to indicate that we are lacking in knowledge of fundamental factors.

The following work is an attempt to uncover such fundamental factors. The work has been divided into four parts: (1) the study of the reducing agent with a constant amount of alkali; (2) and (3) the effect of variation in the amount of alkali upon reduction with the two agents commonly used by clinical pathologists, formalin and potassium oxalate; and (4) the study of an effect upon the reducibility of gold chloride immediately following alkalization, which I found at ranges below neutrality.

I. THE EFFECT OF VARIATION IN THE AMOUNT OF REDUCING AGENT UPON THE COLOR OF THE SOL, RATE OF REDUCTION, AND TEMPERATURE OF REDUCTION

Technic

In the work recorded in connection with this point, as well as in that subsequently given in this paper, a 0.01 per cent solution of chloroauric acid ($HAuCl_4 \cdot 4H_2O$), was reduced in Pyrex Erlenmeyer flasks. The stock solutions from which this dilution was obtained were made by dissolving a 1-g. ampule, as delivered by the manufacturer, in 100 cc. of distilled water, and this was assumed to be a 1 per cent solution. The secondary sodium phosphate used was "Baker's Analyzed" ($Na_2HPO_4 \cdot 12H_2O$). As the work has been carried on over a considerable length of time, the distilled water was not uniform throughout. Earlier in the work artesian

well water, once distilled in a continuous block tin still, was used. Later, the water used was from the city mains, twice distilled from glass. Still later, the water was from a triple still run by steam, twice distilled from glass with permanganate (1). Under the optimum conditions each gave gold which rated as clear orange gold. Water which would not give this result was discarded. The water is undoubtedly one factor in the clarity of the sol and the criterion of a "clear orange sol" is not an absolute one. Many of the "clear orange sols" would probably not have matched one another by reflected light. The relative results, however, have been consistent.

In studying the effect of variation in the amount of reducing agent upon the color of the sol, the three reducing agents, formalin, potassium oxalate, and glucose, were used. The last reducing agent was included because it

TABLE 1

Effect of variation in the amount of reducing agent used upon the color of colloidal gold

POTASSIUM OXALATE		GLUCOSE		FORMALIN	
1 per cent	Color	4 per cent	Color	1 per cent	Color
cc.		*cc*		*cc.*	
0.50	Purple	0 0	Purple	0 05	Colorless
0.65	Orange	0 15	Orange B	0.1	Blue-red
1.0	Orange	0.2	Orange	0.2	Blue-red
2 0	Orange	0 6	Orange	0 3	Orange B
3.0	Orange B	1.0	Orange	0 4	Orange
4.0	Blue-red	3 0	Orange B	5 0	Brownish, blue-red
		5 0	Blue-red		
		7.0	Turbid blue-red		

is reputed to give gold of an entirely different color from the others (6). The reducing agents were neutral and the amount of alkali used in each series was constant, but was not necessarily the same in different series. In the work recorded in table 1 the gold chloride was added to the boiling oxalate and alkali mixture; the formalin was added to the boiling gold chloride and alkali mixture; and in the series made with glucose, all reagents were mixed and then heated to boiling. With appropriate adjustment of the alkali content, however, the order in which the reagents are mixed can be varied. The series run with potassium oxalate contained 0.018 per cent of hydrated secondary sodium phosphate, that run with formalin contained 0.3 per cent, and that with glucose 0.08 per cent of phosphate. Colors of the gold sol were recorded as: blue, purple, blue-red, orange-blue (orange with a tinge of blue, especially noticeable at the angles of the flask, abbreviated to orange B), and orange. The orange-blue is darker than orange and might perhaps be called cardinal. The several

series given in table 2 were not run simultaneously, but are a collection that have the common quality of 0.0375 per cent crystallized secondary sodium phosphate. The colors recorded are the result of comparison within the individual series. As a rule, the same run of distilled water was used in a series. The results recorded in table 3 were obtained by mixing the reagents and heating them simultaneously in a water bath.

TABLE 2

Showing that with a given degree of alkalinity there is an optimum range in the amount of reducing agent which will produce orange colloidal gold with regularity

OXALATE, 1 PER CENT	TRIAL				
	1	2	3	4	5
cc.					
0.50	Lavender	Blue	Blue	—	—
1 00	Purple	Purple	Purple	Blue-red	—
1 25	Blue-red	Blue-red	Blue-red	Blue-red	—
1 50	Blue-red	Blue-red	—	—	—
1 75	Orange	Blue-red	—	—	—
2 00	Orange	Blue-red	Orange B	Orange B	—
2.50	Orange	Orange	Orange	Orange	Orange
3 00	Orange	Orange	Orange	Orange	Orange
4 00	Orange	Orange	Orange B	Orange	Orange B
5 00	Purple	Orange B	Orange B	Orange	Orange B

TABLE 3

Temperature of formation of colloidal gold in relation to amount of reducing agent present

GLUCOSE	PHOSPHATE	GOLD CHLORIDE	TEMPERATURE
per cent	*per cent*	*per cent*	*degrees C.*
0.28	0.075	0.01	60 to 63
0.12	0.075	0.01	70 to 71
0.04	0 075	0 01	78 to 81
0.016	0.075	0 01	78 to 96
0.008	0.075	0.01	99 to 100

Results

It was found that at a suitable degree of alkalinity, if the quantity used of each of the three reducing agents is increased from an amount insufficient to reduce the gold chloride completely, a scale of colors in the gold sol may be obtained ranging through pale lavender, dark blue, purple, blue-red (due to incomplete reduction), to clear orange free from blue. With still further increase in the amount of reducing agent, the gold sol tends to be blue-red and finally, turbid. With respect to formalin this finding was

early reported by Zsigmondy (15) and was recently repeated by Iwase (8). The line of demarcation between the amount of reducing agent necessary to produce clear orange sol and that which will only produce a blue-red is, for a given degree of alkalinity, well defined. The color at this limit may, however, come slowly, and repeated reheating of the medium may be required. A rather wide range exists over which orange gold sol is produced (table 1). From the work recorded in the tables and many other series not recorded, the generalization may be made that, contrary to the prevailing idea that the color of the sol is intrinsic to the reducing agent, each of the reducing agents may be made to produce the same quality of gold when appropriately handled. With each clear orange gold sols could be made, which showed less differences in color and clarity, one from another, than were produced by variation in the amount used of any one reducing agent.

It was found that orange gold sol was most consistently produced when the amount of reducing agent approaches the minimum necessary for reduction (table 2).

These results were, on the whole, obtained with the use of secondary sodium phosphate as the reducing agent, which, because of its buffer value, gave more easily controlled results. Enough work was done with the substitution of sodium hydroxide and potassium carbonate, the two alkalizing substances heretofore used in making colloidal gold, to see that the relationship between the color of the gold sol produced and the amount of reducing agent used was independent of the alkalizing reagent.

With increase in the amount of reducing agent, the speed with which a clear orange was obtained increased and the temperature at which it could be obtained decreased (table 3).

II. THE RELATION OF ALKALINITY TO THE PRODUCTION OF GOLD SOL WITH FORMALIN

Euler and Lövgren (7) found that the velocity constant of the reaction $2HCHO \rightarrow HCOOH$ at 50°C. varies from 0.001 to 0.0929 through a range of pH 11.20 to 12.97. It would seem probable that the successful production of colloidal gold from gold chloride would be influenced by the effect of hydrogen-ion concentration upon the oxidation potential of formalin. A tabulation, incidentally introduced in an article by Wright and Kermack (14), shows that with a variation in the amount of formalin and potassium carbonate used in making colloidal gold, there was a central optimum area, as does a paper by another author who also does not relate his findings to pH. A comparison of the amounts of formalin and alkali recommended in some of the standard formulas for making colloidal gold (table 4), in which definite amounts of both reagents are stipulated, would not, however, suggest any definable relationship. Since it would appear from the

preceding data that clear orange gold sol is obtained with the greatest regularity when the amount of reducing agent used is near to the least amount necessary for complete reduction of the gold chloride, a recognition of the relationship between the activity of the reducing agent and the degree of alkalinity of the medium in which reduction takes place would seem to be desirable. Following is a study of the effect of variations in the amount of alkali present upon reduction of chloroauric acid to colloidal gold by formalin using sodium hydroxide, potassium carbonate, and secondary sodium phosphate. The three alkalies were chosen in the hope that their use might shed some light upon the mechanism of the reaction, since one had no buffer value and the other two exerted their buffer effect in different ranges.

TABLE 4

Comparison of the relative amounts of formalin and potassium carbonate used in standard methods for making colloidal gold

Using 10 cc. of 1 per cent chloroauric acid in 1000 cc. of water

1 PER CENT K_2CO_3	1 PER CENT FORMALIN	TEMPERATURE OF REDUCTION	AUTHOR
cc	*cc.*	*degrees C.*	
14 to 16	10	90 to 95	Lange
14	5	90	Levinson
14	10		Wright and Kermack
16	6	100	Cockrill
20	2.25	92 to 95	Stitt
20	10	75	Breuer

Technic

The pH determinations were made with indicators according to Clark except that double strengths of the dyes were used to avoid the masking effect of the color of the colloidal gold. The standard buffer solutions were obtained through the courtesy of Dr. Clark's laboratory. These were in intervals of 0.2. The readings were approximated to 0.1 by interpolation. All determinations of pH of gold chloride solutions were made at an interval of more than five minutes after the addition of the alkali. Samples of 50 or 100 cc. of the gold chloride solution with the alkali to be tested were brought to boiling, upon which the formalin was added with mixing by agitation. Where sodium hydroxide and secondary sodium phosphate were used, the differences between the pH of the mixtures of gold chloride and alkali at 100°C. and at room temperature were negligible. When potassium carbonate was used, however, the differences were considerable, owing to loss of carbon dioxide. Where more than a relative accuracy was desirable, as in the work recorded in table 8, the pH of the alkalized gold

chloride solution was taken at boiling point. Since in the course of time, from twenty minutes to eighteen hours, gold chloride will change to orange sol with a smaller amount of formalin than is necessary to reduce it in a few minutes, a limit of five minutes was placed upon the time of reduction, in order to facilitate the work. In the more accurate work with secondary sodium phosphate, recorded in tables 7 and 8, the time interval was set between 4½ and 5 minutes. At each degree of alkalinity of the gold chloride chosen, trials were made with increasing amounts of reducing agent until a clear orange was obtained within the required time limit. This often involved a long series of determinations, especially at points of alkalinity at which the activity of the reducing agent was low. Only the greatest amount of reducing agent that did not produce orange sol, and the least amount tried that would produce it in the given time, are recorded, except in the case of data given in table 5. Other series than the ones given were run.

The amount of alkali used and the minimum amount of formalin required

Potassium carbonate. A series using potassium carbonate as the alkali is given in table 5.

It will be noted, first, that successful gold was not made by this method with 10 cc. of 1 per cent carbonate solution to 1000 cc. of 0.01 per cent chloroauric acid, which gave an initial pH of 6.0 to 6.2, nor with 20 cc., which gave, initially, a pH of 9.0. Secondly, that with 11, 12, and 15 cc. of carbonate, which with the gold chloride gave before boiling pH 6.8 to 8.4 and with which successful gold was produced, there was the same tendency, brought out in the first article in this series, to produce bluish-orange, purple, and turbid golds, as the optimum amount of reducing agent was exceeded. Thirdly, it will be noted that, as the amount of alkali was increased, the amount of formalin necessary to produce reduction in approximately five minutes decreased as follows: 11 cc. of 1 per cent carbonate to 7 cc. of 1 per cent formalin solution; 12 cc. of 1 per cent carbonate to 4 cc. of 1 per cent formalin solution; 15 cc. of carbonate to 2 cc. of 1 per cent formalin solution.

In comparing these results with the relative amounts of formalin and carbonate called for in the standard methods given in table 4 (3, 5, 9, 10, 11, 14), it is evident that considerably more formalin is stipulated in these than proved to be optimum in the above series. In the formulas which called for from 14 to 16 cc. of carbonate, the range of formalin added is 5 to 10 cc., whereas, with 15 cc. of carbonate, the optimum as given in table 5 would seem to be 2 to 2.4, 4 cc. being apparently more than the optimum as it gave a blue-orange. Of course, the temperature at which the reducing agent was added is lower in two of these formulas, being 90° to 95°C., which, as has been previously indicated, would require a greater amount of reduc-

ing agent. With 20 cc. of carbonate solution, which in the above series was unsatisfactory, Stitt (11) and Breuer (3) both succeeded in making colloidal gold. By Breuer's method the gold chloride is added to the carbonate at 75°C. immediately before reduction with formalin, and in the method given by Stitt, the gold and carbonate are added at 60°C. and are

TABLE 5

Effect of variation of potassium carbonate on amount of formalin necessary to produce colloidal gold within approximately five minutes

To 1000 cc. of 0.01 per cent chloroauric acid

1 PER CENT K_2CO_3	pH AFTER ADDING CARBONATE	1 PER CENT FORMALIN	QUALITY OF GOLD
cc.		*cc*	
10	6.0–6.2	20	Purple
		40	Blue-red
		60	Blue-red
		100	Turbid purple
11	6.8	6	Orange in 6 minutes
		7	Orange in 7 minutes
		8	Orange in 2 minutes
		11	Orange in 2 minutes
		20	Blue-red
12	6.8	3	Did not turn in 5 minutes
		4	Orange in 5½ minutes
		5	Orange in 4 minutes
		6	Blue-red
		8	Orange in 3 minutes
		10	Blue-red
15	8.4	2	Orange in 5½ minutes
		2.4	Orange in 4 minutes
		4	Orange, slightly blue
20	9.0	1	Purple-red
		1.4	Purple-red
		3	Blue-red
		4	Blue-red

then brought up to 92° to 95°C., when the formalin is added. A decreased activity of the formalin at the lower temperatures used by Breuer and Stitt may account for their success in making colloidal gold with the larger amount of potassium carbonate.

Sodium hydroxide. As sodium hydroxide is an alkaline substance of great strength and no buffer value, it is somewhat difficult to handle in such

a series of reductions as the foregoing. Such series run with sodium hydroxide as the alkalizing agent showed a decrease in amount of formalin with an increase in the amount of hydroxide added. Owing, however, to the rapid increase in alkalinity caused by addition of sodium hydroxide, the range of amount of sodium hydroxide taken, through which colloidal

TABLE 6

Effect of variation in the amount of sodium hydroxide solution upon the activity of formalin in the reduction of chloroauric acid to colloidal gold within five minutes

To 1000 cc. of 0.01 per cent chloroauric acid

N/10 NaOH	INITIAL pH	COLLOIDAL GOLD pH	1 PER CENT FORMALIN	TIME
cc.			cc.	
14	8.2 to 8.4	6.6	1.4	Orange in 3½ minutes
13.5	7.0		1 4	Did not turn in 5 minutes
12.5	7.0 to 6.8	5 6 to 5.4	4.0	Orange in 2 minutes
12.0	6.4		4 0	Did not turn in 5 minutes

TABLE 7

Showing variation in the amount of formalin required to produce colloidal gold in approximately five minutes at varying degrees of alkalinity produced by secondary sodium phosphate

To 1000 cc. of 0.01 per cent chloroauric acid

1 PER CENT Na_2HPO_4 $12H_2O$	INITIAL pH	FINAL pH	AMOUNT OF 1 PER CENT FORMALIN ADDED	
			Did not give gold in 4½ min.	Gave gold sol in 5 minutes
cc			cc.	cc.
300	8.2	8.2	1.5	1.6
160	7.5	7.2	1.8	2 0
120	7.3	7.0	2 4	2.5
80	7 0	6 8	5 0	5.5
70	7.0	5 4	5.0	5.5
60	6.9	5.4 to 4 8	7.0	8.0
50	6.8	5.4 to 4 8	10.0	11.0

gold could be made, was narrow. In the following, two amounts of formalin were used and the amounts of sodium hydroxide, necessary to add before reduction took place within five minutes, were determined with the initial and final pH. Results are given in table 6.

Secondary sodium phosphate. By the use of secondary sodium phosphate, two of the difficulties which were met with the foregoing reagents were avoided; a considerable buffer value was introduced, which was not given

by sodium hydroxide, and the apparent irregularities in result due to the loss of carbon dioxide from the carbonate radical were obviated. The results, given in table 7, again indicate an inverse relationship between the amount of alkali taken and the amount of formalin necessary for reduction of gold chloride to colloidal gold.

Relation between hydrogen-ion concentration and the activity of formalin in the reduction of gold chloride to colloidal gold

The foregoing data would seem to indicate clearly that with an increase in the amount of alkali used there is a decrease in the amount of formalin

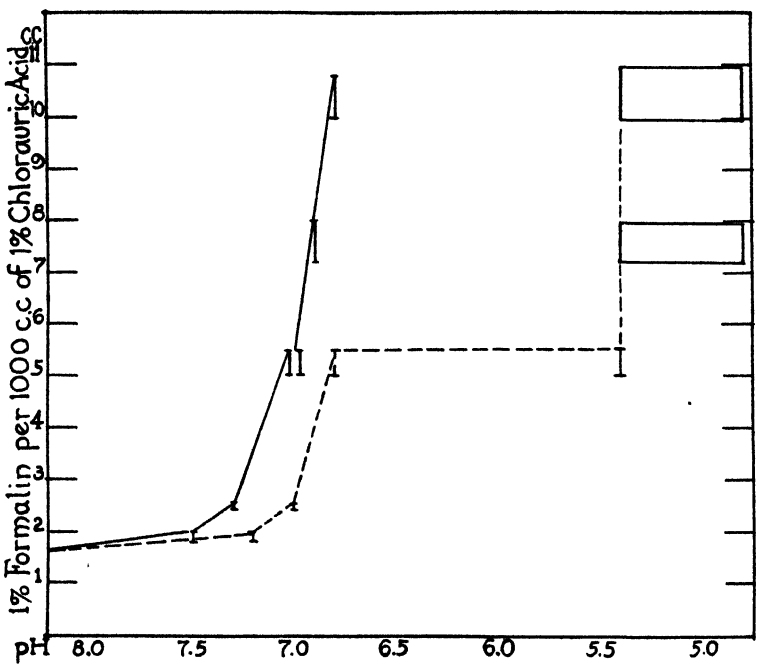

FIG. 1. THE AMOUNT OF FORMALIN PRODUCING COLLOIDAL GOLD IN FIVE MINUTES RELATED TO pH

necessary to reduce the given solution of chloroauric acid to colloidal gold. It would seem to be a matter of interest to determine whether this increased efficiency is due to what Clark (4) calls the "quantity factor" of the alkali, or to the "intensity factor." In other words, is the hydrogen-ion concentration at some stage of the reaction the determining factor? When the results given in table 7 are plotted with respect to the initial and final pH and the amount of formalin used to effect reduction in five minutes (figure 1), the curve obtained for the initial pH is, within the errors of the technic used, a smooth one, while the graph for the final pH is irregular with re-

spect to the amounts of formalin required. This suggestion, that the effective factor is the hydrogen-ion concentration at or near the beginning of the reaction, is supported when the curves obtained with secondary sodium phosphate are plotted in conjunction with the data obtained by the use of potassium carbonate and sodium hydroxide, an alkali with no buffer value, as is done in figure 2. To this graph were also added all other values obtained in which an approximate 5-minute period and 100°C. temperature was used, and in which the initial and final pH are determined. No high degree of accuracy is claimed for this comparison, as the determinations

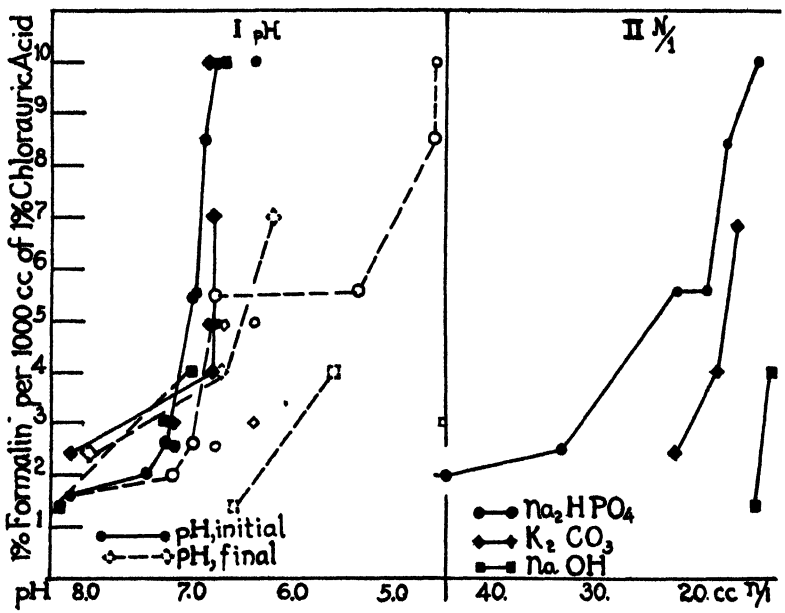

FIG. 2. THE AMOUNT OF FORMALIN PRODUCING COLLOIDAL GOLD RELATED RESPECTIVELY TO (I) THE INITIAL AND FINAL pH PRODUCED BY SECONDARY SODIUM PHOSPHATE, SODIUM HYDROXIDE, AND SODIUM CARBONATE, AND (II) THE AMOUNT OF ALKALI USED IN TERMS OF "NORMAL" VALUE

were made at wide intervals of time with unidentical solutions and the pH determinations in the case of the graph representing the results with potassium carbonate carry the inaccuracy due to loss of carbon dioxide. The points of the initial pH, however, do not fall more than pH 0.2 from their mean curve, except in one instance in which potassium carbonate was used. The points of final pH are widely scattered. If, on the other hand, the "normal" value of the three alkalies used is substituted for the pH value, curves are obtained which are independent of one another, but are situated parallel and related according to the strength of the alkali (figure 2).

To check these results further, an attempt was made to find the minimum

amount of each of the following three alkalies—sodium hydroxide, potassium carbonate, and secondary sodium phosphate—which would give orange sol with 0.14 cc., 0.3 cc., and 1.8 cc. of 1 per cent formalin to 100 cc. of gold chloride solution. With the given amount of formalin, the amount of alkali added to the gold chloride solution was increased until a clear orange sol was obtained in approximately five minutes. The pH of the gold chloride was determined at boiling point immediately before addi-

TABLE 8

Relationship of initial and final pH and combining value of alkali used to amount of formalin causing reduction in 100 cc. of 0.01 per cent chloroauric acid

AMOUNT OF 1 PER CENT FORMALIN	N/10 ALKALI		INITIAL pH	FINAL pH	TIME OF REDUCTION AND QUALITY OF GOLD
cc.		cc.			
0.14	NaOH	1 40	8 4 to 8 2	6 6	Orange gold in 3½ minutes
		1 35	7.0		No reduction in 5 minutes
0.14	Na_2HPO_4	11 2	8 1 to 8 2	8.1	Orange gold in 6 minutes
		8.4	8 0		Orange gold in 7 minutes
0.3	NaOH	1.36	7 0 to 7.3	4 6 to 4.8	Orange
		1.32	6 4		Lavender
0.3	K_2CO_3	1 74		6.8	Orange
		1.6	6.6		Blue-red
0.3	Na_2HPO_4	1 95	6 8	6.4	Orange
		1.67	6.6		Did not turn
1.0	NaOH	1.39	6 7	5 2–	Orange
		1.38	6 4		Blue-red
1.0	K_2CO_3	1.44	6.8	5 2–	Orange
		1 28	6.4		Blue-red
1.0	Na_2HPO_4	1.40	6 4	5.2–	Orange
		1.28	6 2		Did not turn

tion of the reducing agent. As NaH_2PO_4 gives a pH below the range dealt with in this series, it was held that the reaction $Na_2HPO_4 \rightarrow NaH_2PO_4$ only need be considered. A molar solution of Na_2HPO_4 has therefore been rated as a normal solution. Each of the three series was run with the same gold chloride and formalin solutions, but different solutions may have been used for different series, so the three series are only strictly comparable within themselves (table 8). These data, when taken in conjunction with those previously given, would seem to indicate that hydrogen-ion concen-

tration is the factor which determines the amount of formalin necessary to produce colloidal gold from gold chloride, and that it is the hydrogen-ion concentration at or near the beginning of the reaction which is the determinant.

III. RELATION OF ALKALINITY TO REDUCTION OF GOLD CHLORIDE TO COLLOIDAL GOLD BY OXALATE

What data we have on the optimum relationship between the amounts of oxalate and the alkalinity of the medium is derived from standard formulas devised for preparing gold sol for clinical use. A comparison of these indicates no relationship. According to Bacon (2), the oxalate radical increases its ability to be oxidized under the influence of sunlight with increase in acidity. As reduction with oxalate proceeds, the medium, of course, decreases in acidity, owing to destruction of the oxalic acid radical.

TABLE 9

Variation in the amount of oxalate required to reduce gold chloride to colloidal gold with variation in amount of sodium hydroxide used

N/10 NaOH	1 PER CENT POTASSIUM OXALATE	INITIAL pH	FINAL pH	QUALITY OF THE GOLD
cc.	*cc.*			
0.5	0.6	3 2	—	Blue-red
0.5	0.75	3 2	6 8	Brilliant orange
1.1	1.75	5 2	—	Blue-red
1.1	2.0	5.2	7.0	Brilliant orange

As the circumstances of oxalate reduction are probably the opposite of those with formalin, it seemed probable that the results with oxalate reduction would be a mirror image of those already obtained with formalin, provided that the gradient obtained with formalin was due to increase in the oxidation–reduction potential of the formalin under increased pH. Since the increase in alkalinity of the medium during oxidation of the oxalate would tend to check reduction, we would, as with formalin, expect to find a relationship between the amount of oxalate necessary for reduction in unit time and the initial pH of the medium. If, however, the gradient was due to an effect of alkalinity upon the gold chloride, it would be conceivable that results with oxalate would be similar to those obtained with formalin.

A short series run with sodium hydroxide and two with secondary sodium phosphate are given in tables 9, 10, 11. In the series given in table 10, the gold sol was made by adding the gold chloride to the boiling mixture of alkali and oxalate following the usual method. This necessitated determining the initial pH from a blank of the gold chloride and alkali. This

determination probably gave the pH at which reduction commenced, since with the amounts of reducing agent used there was no evidence of reduction until after the gold salt had been added and mixed. The method, however, was considered unsatisfactory and in table 11 the oxalate was added

TABLE 10

Variation in the minimum amount of oxalate required to reduce 100 cc. of 0.01 per cent chloroauric acid to colloidal gold in approximately five minutes with variation in the amount of secondary sodium phosphate

Gold added last

1 PER CENT PHOSPHATE	1 PER CENT OXALATE	INITIAL pH	FINAL pH
cc.			
0	Did not give a clear gold	Less than 2.8	
0.5	0 7 cc. or less, more than 0 6 cc.	2.8 to 3.6	4 0
1 5	0 75 cc. or less, more than 0 7 cc.	2 8 to 3.6	6 8
2 0	0 75 cc. or less, more than 0.7 cc.	2 3 to 3.8	6 8
3.0	1 0 cc. or less, more than 0.75 cc.	5.6	6 9
4 0	1 3 cc. or less, more than 1 0 cc.	5 7	7 1
6 0	2.0 cc. or less, more than 1.8 cc.	6 8	7.3
8 0	3 0 cc. or less, more than 2 75 cc.	7 2	7 8
16 0	Did not give a clear gold	7 6	

TABLE 11

Variation in the amount of oxalate required to reduce 100 cc. of 0.01 per cent chloroauric acid to colloidal gold in approximately five minutes with variation in the amount of secondary sodium phosphate

Oxalate added last. (Series 3 in figure 3)

1 PER CENT PHOSPHATE	1 PER CENT OXALATE	INITIAL pH	FINAL pH
cc.			
4.5	1 5 cc. or less, more than 1 3 cc.	6.6	7.1
5 0	1 5 cc. or less, more than 1 3 cc.	6 6	7.2
6 0	2.0 cc. or less, more than 1 8 cc.	6.7	7 4
8.0	4.0 cc. or less, more than 3 8 cc.	7.1	7.5
12.0	5 3 cc. or less, more than 5 0 cc.	7.3	7.6
14 0	7 to 10 cc. gold purple, later changed to blue-red		

to the hot gold chloride and phosphate mixture. With this modification the production of colloidal gold could not be carried down nearly so far into the acid side.

The first few series run indicated the relationship of an increase in effectiveness of the oxalate to produce gold sol with an increase in acidity of the medium. The expected relationship of the effective pH being some-

where near the beginning of the reaction, as was found to be the case with formalin, did not appear. Many series were run over a considerable length of time, during which fresh solutions had been made up with different batches of distilled water and with slight variations in technic, but apparently with discordant results. At last all series were plotted in terms of initial and final pH and the amount of oxalate which produced gold sol in 5 minutes. The amount which would not produce reduction in 5 minutes is indicated by a line attached to the initial pH, which is indicated with the solid circles. This is given in figure 3. This charting indicates that, in-

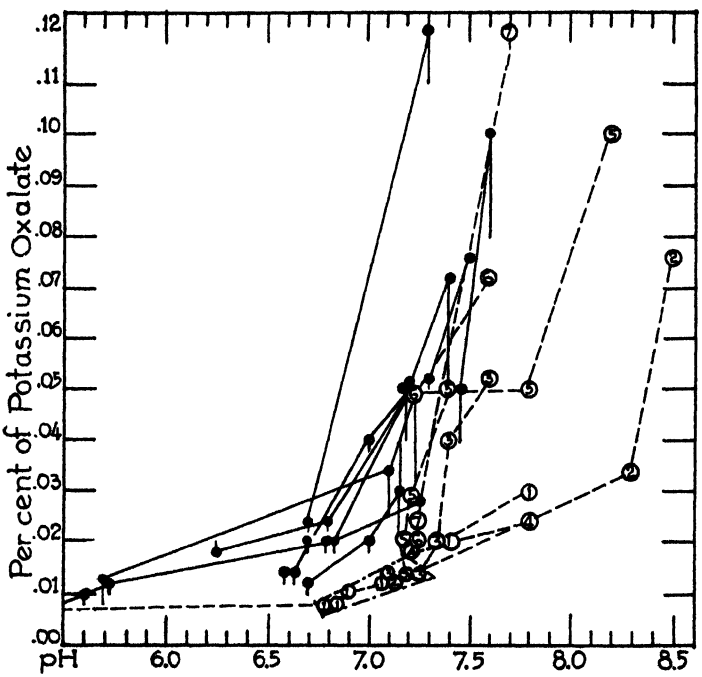

FIG. 3. SEVEN SERIES IN WHICH THE OXALATE REQUIRED FOR REDUCTION IS PLOTTED AGAINST THE INITIAL AND FINAL pH

stead of the initial pH, it is the final pH that is the uniform factor up to pH 7.3, more or less. After this the final pH is scattered and the initial pH shows a fair degree of alignment. The two points which are distinctly out of alignment belong to a series in which the technic was such that reduction began at a lower temperature and, therefore, form an exception.

As was done with formalin, a unit of oxalate was taken in this region in which the final pH seemed to be the determining factor; 1 cc. of 1 per cent to each 100 cc. of chloroauric acid was used, and the amount of the three alkalies—sodium hydroxide, potassium carbonate, and disodium hydrogen phosphate—was varied, until orange gold sol formed in 4½ to 5 minutes.

With phosphate, four determinations were made in which orange gold sol was formed in the required time. The amount of phosphate varied as much as 20 per cent. The initial pH was, respectively, 5.5, 5.8, 6.2, and 6.4. The final pH was in each instance pH 6.8 to 6.9. The mixtures which would not give orange gold in the required amount of time had a final pH of 7.0 or more. The results with sodium hydroxide and potassium carbonate were scattered. I do not believe that any of these pH determinations with oxalate as the reducing agent can be repeated, except with phosphate, since a certain amount of buffer value is necessary to damp the effect of loss of carbon dioxide which is formed during the reaction, and the buffer value of potassium carbonate over this range is low.

IV. A ONE-WAY EFFECT OF CHANGE OF HYDROGEN-ION CONCENTRATION UPON GOLD CHLORIDE

The rate of change of color of gold chloride upon acidification and alkalization

In the course of determining the pH of mixtures of gold chloride and secondary sodium phosphate, it was noted that there was a considerable time interval before the change of color, which occurs as acid gold chloride is made more alkaline, was finally established. This color change was studied with relation to change in alkalinity and acidity as follows.

If 2 cc. of normal hydrochloric acid are added to 100 cc. of approximately 0.01 per cent chloroauric acid, there is a well-defined increase in the depth of the yellow color which in a colorimeter shows approximately a relationship of 2:3 between the depth of the columns of acidified and unacidified fluids. When, on the other hand, alkali is added, the yellow color disappears and, finally, with the further addition of alkali, it is replaced by a bluish tinge which in turn disappears with the addition of acid, and with further addition of acid the yellow color reappears. The change in color when the solution is made alkaline is not instantaneous. There is a definite time element involved which is greater than that which would be necessary for the complete mixing of the ingredients. This is not true of the reverse color change upon the addition of acid.

To correlate the change of color and the pH, secondary sodium phosphate was added in varying amount to a 0.01 per cent solution of gold chloride. After 10 minutes, when the color change appeared to be established, a comparison was made of the resulting colors through a depth of three inches and the hydrogen-ion concentrations were read approximately with indicators. There was a gradual decrease in intensity of color with increase of pH from 3.4 to 6.4. The observer failed to discern any yellow at pH 6.6, although a faint trace was recorded for pH 6.4. When, however, the solution of gold salt was made eight times as strong, there was an appreciable amount of yellow remaining at pH 7.4. The apparent disappearance of the yellow color at the lower pH in the more dilute solution

is probably real and due to a greater degree of hydrolyzation in the weaker solution under the influence of the same degree of alkalinity.

To make a rough measurement of the time taken to establish the color change, a solution was used containing 8 cc. of 1 per cent gold chloride per 100 cc. of water; to this secondary sodium phosphate was added, and the color was compared with a blank of the gold chloride solution to which no phosphate had been added. It was found that after 2 minutes the depth of color of the alkalized gold chloride was five-ninths of that of the blank, and after 3 minutes it was three-ninths of the blank. After 30 minutes there was no further change, indicating that a period between 2 and 3 minutes is required for the establishment of the change of color with an 0.08 per cent solution of gold chloride in the presence of insufficient alkali to change the color completely. This time element appeared to be of the same degree of magnitude for weaker solutions of gold chloride.

Upon attempting to see how soon the pH was established with these comparatively slow color changes, it was found that, when bromothymol blue was added to 0.08 per cent chloroauric acid solution immediately after alkalization, the color of the indicator was promptly destroyed, whereas, if a time interval of 5 minutes was allowed, the color of the indicator held for four hours or longer. As no color destruction was evident upon addition of the indicator to the gold chloride solution before adding the alkali, this destruction of the color of the indicator would seem to be due to some increased activity of the gold chloride in the process of changing from the acid to the alkaline state. This phenomenon was elicited with 0.5 cc. of the usual 0.04 per cent water solution of bromothymol blue, used in pH colorimetric determinations, to 5 cc. of the 0.08 per cent gold chloride solution, after the addition of enough phosphate solution to bring the reaction up to pH 6.8 to 7.4. It could also be demonstrated with the 0.01 per cent chloroauric acid solution, but it was necessary to use less indicator. The effect was masked by more than 0.1 cc. of indicator in 5 cc. of 0.01 per cent of gold chloride solution. Bromocresol purple, thymol blue, cresol red, and bromophenol blue were similarly destroyed, if added to the 0.08 per cent gold chloride solution immediately after alkalization. In the tubes in which the color was destroyed there gradually appeared faint pink or lavender coloration due to the formation of colloidal gold.

This retarded change of color with a concomitant instability of the salt solution upon alkalization did not occur upon acidification.

Effect of time interval after alkalization upon the formation of colloidal gold

This transitory period of sensitiveness of the gold salt to reduction after alkalization, observed in an attempt to use indicators, was studied with potassium oxalate as the reducing agent. It was examined with reference to range of pH and time interval after alkalization.

To study the range of acidity through which this effect might be demonstrated, a series of mixtures of secondary sodium phosphate and 0.01 per cent "gold chloride" was made and the solutions were allowed to stand for more than three minutes before bringing to the boiling point. At the boiling point 1 cc. of 1 per cent potassium oxalate per 100 cc. of solution was added to each. A second series was made containing the same proportions of phosphate, oxalate, and gold chloride, but in order that reduction might take place during this transitory effect of alkalization upon the gold chloride, the gold chloride was added last after the rest of the ingredients had come to the boiling point. These results are tabulated in the first part of table 12. In the course of reduction of gold chloride by potassium oxalate, the increase in alkalinity due to destruction of the oxalate radical also contributes to the alkalization of the unreduced gold chloride. The final pH, therefore, is the critical pH and it, rather than the initial pH, is given in the tabulation. In the series in which reduction took place, while, presumably, this transitory effect of the alkalization of the gold chloride held, a clear brilliant orange gold sol was produced. In the series in which there was a time interval allowed between alkalization and reduction with potassium oxalate, a clear gold solution was obtained when the final pH reached 6.8; but, as the final pH decreased, solutions of greater turbidity were obtained.

TABLE 12

Effect of the time interval after alkalization

1. With varying amount of alkali

$M/10$ Na_2HPO_4	FINAL pH	OXALATE ADDED LAST	GOLD ADDED LAST
1 2 cc. per 100	6.8	Clear orange	Clear orange
0.8 cc. per 100	6.7	Bluish red, slightly turbid	Clear orange
0.6 cc. per 100	6.5	Blue-red, turbid	Clear orange
0.4 cc. per 100	6.4	Precipitated	Clear orange

2. With variation of the time interval between addition of gold salt to alkali and reduction

TIME INTERVAL	QUALITY OF GOLD	FINAL pH
Gold added after oxalate	Clear orange	6.4
Oxalate added 5 seconds after gold	Clear orange	6.4
Oxalate added 15 seconds after gold	Slightly turbid blue-red	6.4
Oxalate added 15 seconds after gold	Blue-red, more turbid	6.4
Oxalate added 30 seconds after gold	Turbid purple	6 4
Oxalate added 1 minute after gold	Precipitated	6.4

The effect of the time interval was next tested, using the least amount of phosphate in the preceding series, 0.4 cc. of $M/10$ per 100 cc., which,

when the oxalate was added to the gold salt already mixed with the phosphate, gave a heavy precipitate. The phosphate and water were brought to boiling, the gold chloride was added, and at varying intervals after the addition of the gold salt, the oxalate was added. The results are given in the second part of table 12. After an interval of 1 minute between the addition of the gold chloride and the reducing agent, the gold was heavily precipitated; after an interval of 30 seconds there was marked turbidity; with an interval of 15 seconds the turbidity was much less; and when there was approximately only a 5-second interval, a perfectly clear orange gold equal to the control was obtained.

These results cannot be attributed to inadequate mixing of the reagents, which might be a factor in causing the production of turbid gold, because the clear gold was produced after the shortest interval when the difficulties of adequate mixing were greatest. The production of the more turbid gold solution with the longer interval cannot be attributed to any effect of the alkali upon the gold chloride during the time that the mixture was kept at 100°C., as highly dispersed gold sol was produced under the same condition at a higher degree of alkalinity. The production of highly dispersed gold sol by means of potassium oxalate, when the final pH is less than 6.8, seems to be definitely associated with reduction during a short time interval after the alkalization of the gold salt.

In the series in which reduction took place after this time interval had elapsed, and in which turbid gold solution was formed, there was a distinct lag before any change of color indicating the beginning of reduction occurred, as compared with the series in which the reducing agent was added before or during this transitory effect following alkalization of the gold chloride and in which colloidal golds of high dispersion were obtained. An attempt was made to relate this effect to the surface of the container, but the results were negative.

DISCUSSION AND SUMMARY

By the introduction of the use of secondary sodium phosphate in place of sodium carbonate or sodium hydroxide, a greater degree of consistency has been developed in the production of gold sol by the methods of reduction of gold chloride with potassium oxalate and formalin. This finding would seem to be due to the greater effectiveness of secondary sodium phosphate in maintaining an optimum pH over the range through which these reducing agents function in the reduction of gold chloride to gold sol.

With the use of the three reducing agents, potassium oxalate, formalin, and glucose, it was found that, at appropriate degrees of alkalinity, colloidal orange golds of the same quality were produced, when the amount of reducing agent used did not greatly exceed the minimum amount required for reduction. With the use of an amount of reducing agent near to the

minimum, consistent results were obtained. As this amount was exceeded, the sol tended to become blue-red and turbid. The color and quality of the sol would seem to depend upon the attainment of a certain intensity of reduction by the respective reducing agents and not upon the kind of reducing agent used, which is contrary to the prevailing idea (12).

By varying the amount of alkali and reducing agent it was found that the minimum amount of formalin that would give orange sol in approximately five minutes at 100°C. varied from 1.5 units to 10.0 units through a range of initial pH of 8.2 to 6.8, following a curve suggesting that obtained by Euler and Lövgren for the reaction rate of oxidation of formalin. The failure of big variations in the final pH, which occurred when sodium hydroxide and potassium carbonate were used in place of secondary sodium phosphate and through certain ranges of the phosphate alkalizer, to affect this relationship indicates that it is the pH somewhere near the beginning of the reaction which is effective.

With the use of oxalate as the reducing agent the same relation apparently holds from pH 7.6, where the effectiveness of potassium oxalate as a reducing agent begins to disappear, to approximately pH 7.2, after which some other factor appears which relates the amount of reducing agent required for reduction in a given time to the final pH of the medium. This factor would seem to be the effect of the increase in alkalinity, which the medium undergoes during the destruction of the oxalic acid radical, upon the reducibility of the gold chloride, as discussed below.

It was noted that the loss of color, which chloroauric acid undergoes when made neutral, involved a time element of approximately three minutes, while the appearance of the yellow color upon acidification was apparently instantaneous. It was found that indicator, added to the chloroauric acid immediately after adding alkali, was destroyed; whereas it was not destroyed when added after the change in color was complete, nor with the reverse process of acidifying the colorless gold chloride. It was further found that, if the gold salt is reduced with potassium oxalate immediately after the addition of alkali (secondary sodium phosphate), a highly dispersed colloidal gold can be made at a higher degree of acidity than is possible if the reducing agent is added after this transitory period of instability is passed. This entirely different behavior of the gold salt, when the reaction is changed from the acid to the alkaline side, to that which occurs when the reaction is changed from the alkaline to the acid side, is somewhat difficult to account for. I offer the following suggestion as a possible explanation of the phenomenon. I assume that the formation of $AuCl_4$ from $AuCl_3$ and HCl, or the reverse action, is a time-consuming, possibly nonionic, process. Further, that the yellow color is produced by the presence of the radical $AuCl_3$, either as $AuCl_3$, or as part of the radical $AuCl_4$. The yellow color immediately disappears as $AuCl_3$ is hydrolyzed upon its forma-

tion with the addition of alkali, but as the formation of $AuCl_3$ from $AuCl_4$ is a time-consuming process, and, as we assume that $AuCl_3$, whether free or in the radical $AuCl_4$, produces yellow, the disappearance of the color involves appreciable time. With the reverse process of adding acid to the colorless gold salt solution, the ionization of $AuCl_3$ is suppressed by the acid with an immediate return of the yellow color, following which the slower formation of $AuCl_4$ takes place. If this were a fact, it would explain the slow loss of color upon alkalization, and the immediate return with acidification. To explain the temporary period of instability which occurs after alkalization to a pH approaching neutrality, and which does not occur after acidification, it might be assumed that in this shift involving the loss of chloride there is a readjustment of intramolecular tension, which leads to a greater sensitiveness to reduction. As $AuCl_4$ goes over into Cl and $AuCl_3$, there is a state of instability which does not occur when the reverse process takes place, and the forces are such that the radical is being built up.

The production of turbid colloidal solutions when certain optimum amounts of reducing agent are exceeded at any given degree of activity of the reducing agent as determined by the pH, and the production of turbid sols by oxalate when the activity of reduction is increased beyond a certain limit by increased acidity, and by formalin beyond a certain limit of alkalinity, would suggest some common factor. This could be expressed by Zsigmondy's hypothesis, that turbid sols result when the rate of reduction is excessive in relation to the rate of nuclei production, if we had some applicable concept of the mechanism of nuclei production.

If, for the various reasons that Weiser and Milligan (13) have advanced, von Weimarn's theory, that nuclei of gold sol result from the formation of particulate gold hydroxide, is untenable, the concept of nuclei derived from foreign particulate matter would seem to be equally ruled out by the above data. It is to me inconceivable that foreign particulate matter can explain the fact that, with the use of the same solutions and utensils, clear orange gold can consistently be made by adding potassium oxalate to the boiling solution of gold salt and phosphate when a final pH of 6.7 is attained, but that a very turbid sol is formed, presupposing few nuclei, when the phosphate is reduced so that the final pH is 6.4; while, if the same reagents are added in a different order, or with a different time relationship, a highly dispersed sol is again produced with the lesser amount of phosphate. It would seem that this phenomenon introduces the factor of the reducibility of the gold chloride into the question of nuclei formation, as there is evidence that the more highly dispersed gold was formed under conditions which produced decreased stability of the gold salt.

The finding of a relationship between the amount of formalin, or oxalate (except where the above phenomenon comes into play) required for reduc-

tion, and initial pH, together with the fact that as reduction proceeds the change of pH in the medium is such that the oxidation-reduction potential decreases, would suggest the possibility that nuclei formation is determined by the higher oxidation–reduction potential, and that, this initial reduction having taken place, more gold chloride is capable of being reduced, under the influence of the surface attraction of these nuclei, at the lower pressures of reduction produced by the less favorable degrees of alkalinity developed. The findings in the more acid ranges of oxalate reduction are not necessarily inimical to this hypothesis, but certain of my findings with other reducing agents, e.g., sodium tartrate, may be. But the above as a partial explanation will, I think, stand.

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STUDIES IN CELLULOSE DETERIORATION. I

THE AUTOXIDATION OF MANNITOL

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The deterioration of textiles has been shown by numerous investigations to be an atmospheric oxidation process, the speed of which is accelerated by light and influenced by positive and negative catalysts (3, 4, 15). None of the researches has been conducted with a view to establishing the mechanism of the oxidation process. If the proper steps to prevent the deterioration of textiles are to be taken, such knowledge of the reaction is essential. Now, in known oxidation process where prevention of the reaction by small quantities of an inhibitor is possible, the reaction has been shown to proceed by a chain mechanism. Effective inhibition can only be expected if textile deterioration be a reaction involving long chains. These principles of chain processes as applied to deterioration problems have been fully developed by Taylor (19), and will not be repeated here.

Cellulose possesses a molecule chemically similar to the molecules of carbohydrates and polyhydroxy alcohols, in that they all consist of a chain of carbon atoms with attached hydroxyl groups. Consequently, in most of its reactions cellulose behaves as a polyalcohol, a fact which is well recognized (5). Now, in the autoxidation of the analogous substances, inorganic materials exert positive accelerating effects, and Taylor has pointed out that attention should be paid to the influence of such agents in the deterioration of cellulose. The parallelism between the oxidation of cellulose and of related substances in reality seems to be very close. For example, Traube (22) showed originally that mannitol is oxidized by air in the presence of copper salt, and more recently that ferric chloride and alkali cause a great increase in the amount of oxygen absorbed by the solution (24). The oxidation of sugars by air in the presence of sodium ferropyrophosphate has been demonstrated by Spoehr (17, 18). Dhar and his collaborators (14) have many instances of induced oxidations of carbohydrates and alcohols by such inductors as ferrous hydroxide, stannous hydroxide, and sodium sulfite. With cellulose, the atmospheric oxidation proceeds slowly, but can be considerably accelerated by light. Alkali-cellulose,

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however, shows very appreciable absorption of oxygen (26), and Davidson's (6) recent extensive investigation shows the great effect of heavy metals as positive catalysts for the oxygen up-take. Apparently, also, sodium bisulfite present in pressed alkali-cellulose induces the aging of the substrate (25), much as sodium sulfite is able to induce the oxidation of carbohydrates.

The polyhydroxy alcohol, mannitol, has been chosen as typical of a complex molecule related to cellulose, and its autoxidation in the presence of various agents has been studied. The primary purpose has been to determine whether or not the oxidation proceeds by a chain mechanism, for if the oxidation of this simpler molecule proved not to be a chain reaction, then it seemed unlikely that the oxidation of cellulose and other related substances could be a chain process. Reaction rates have been measured by determining the rate of absorption of oxygen from the gas phase, and the usual criteria of chain reactions have been employed to test the character of the oxidation.

EXPERIMENTAL

Apparatus

Two types of apparatus have been used to determine the oxygen absorption rate, a shaker machine and a bubbler apparatus. The former has been described elsewhere (1). Its main parts are a Hulett gas buret (20) connected by a short length of pressure tubing to a reaction vessel which is clamped securely to a shaker device. The latter, operated by a motor-driven eccentric, makes about 260 oscillations per minute. The reaction vessel and shaker device are completely immersed in a large thermostat. To facilitate photochemical work, a hole was cut in the side of the thermostat and covered with a quartz window.

The bubbler apparatus was a modification of one used by Egerton (7); its general principles also have been incorporated in a somewhat similar apparatus by Long and Chataway (13). Its main features are a pump to circulate gas around a closed system, a reaction cell to contain the oxidizable liquid, and a gas buret to indicate the volume of oxygen absorbed.

For circulating the gases, the double action pump described by Spence and Kistiakowsky (16) was employed, with, however, the ordinary type of ground glass valves to control the direction of gas flow. The pump operated at atmospheric pressure to give a flow of about 650 cc. of gas per minute.

The reaction cell was designed to insure complete saturation of the liquid by the gas. As shown in the sketch, figure 1, a Pyrex tube, 3 × 16 cm., closed at one end, was fitted by a ground joint to a glass cap. Attached to the cap was an outlet tube, and also a tube serving for the introduction of liquids into the cell. Likewise, ring-sealed through the center of the cap, a 7-mm. Pyrex tube projected downward. At the end of this down-

tube, a porous alundum plate ("A" in the sketch) was sealed through a hole drilled in its center. A hemispherical cup of Pyrex was sealed around the porous plate. The cell was attached to the apparatus so the circulating gas entered through the down-tube and was broken into fine bubbles as it was forced through the porous alundum.

The bubbler apparatus has certain advantages over the shaker machine, especially in event of gaseous oxidation products, for suitable absorbents for these can be placed in the circulating system. It is superior, also, for

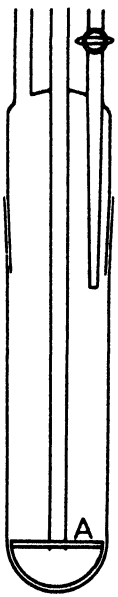

FIG. 1. THE REACTION CELL

photochemical experiments. A vertical type mercury arc is conveniently mounted directly in front of the reaction cell, and for quantum yield work with the uranyl oxalate actinometer, the necessary auxilliary vessel is easily held in position in rear of the reaction vessel. Thus the position of the arc, reaction cell, and auxiliary vessel is readily and definitely fixed, a troublesome problem with a shaker device. The chief defect of the present bubbler apparatus was the difficulty of accurate pressure adjustment during an experiment. Such trouble was due to the rather large total volume of the system, but mainly to the pressure fluctuations resulting from the pressure head built up by the circulating pump.

Materials

The mannite was prepared by recrystallization of a Kahlbaum's product. The solutions were made up by accurately weighing out the desired quanti-

ties and dissolving in the necessary amounts of distilled water. The sodium hydroxide solutions were prepared from a saturated solution of Merck's C. P. sodium hydroxide by diluting to the desired strengths. A solution of ferric chloride was made up to approximately 0.5 molar, and its strength determined by the iodometric method. Portions of this solution were diluted to the desired concentrations as the occasion demanded.

Procedure

In measuring the rate of oxygen up-take with the shaker machine, the general procedure was the following. The apparatus was first filled with tank oxygen, and the solutions were then added to the reaction vessel from calibrated pipettes. These solutions previously had been made up to such concentrations that, when added in the correct amounts to the reaction vessel, the final concentrations of the various components were those desired for the particular experiment. The final total volume was 25 cc. in every case. After adjustment of the pressure in the system to atmospheric, the shaker was started and volume readings, always at atmospheric pressure, taken at suitable time intervals.

With the bubbler system the procedure was necessarily different. The clean dry reaction vessel was first attached to the apparatus by its greased ground joint, and a small thermostat then raised up to immerse the vessel. By means of a Cenco Hyvac pump, the system was evacuated, and then was immediately filled with tank oxygen. The solutions were run into the cell through the attached calibrated burets, a final volume of 25 cc. being employed as with the shaker machine. After adjusting the pressure to atmospheric, the circulating pump was started. The decrease in volume at atmospheric pressure with time gave the rate of oxidation.

RESULTS

The dark reaction

Preliminary experiments showed that no oxygen was taken up by pure aqueous mannitol solutions, but that on the addition of both ferric chloride and sodium hydroxide to the mannitol, absorption of oxygen occurred at an appreciable rate. Under these conditions, no precipitation of ferric hydroxide resulted, because, as Traube and Kuhbier (23) showed, a complex ferrimannite compound formed. The research consequently resolved itself into an investigation of the effect of these inorganic materials on the oxidation rate. As pointed out in the introduction, the deterioration of cellulose is most rapid after treatment with these same agents.

The oxidation by gaseous oxygen of mannitol in the presence of ferric salt and alkali is an auto-accelerating reaction. A typical rate curve is shown in figure 2, in which cubic centimeters of oxygen (at N. T. P.) are plotted against time in minutes. The reaction rate increases with time

until a fairly constant value is reached. Record may be made of the fact that when ferrous sulfate was substituted for ferric chloride, oxygen was taken up immediately on starting the shaking machine, forming a small amount of precipitate in the process. The amount of gas absorbed was about that necessary to oxidize the ferrous iron to ferric. The reaction then proceeded as in those cases where ferric salt was added originally, the same kind of slowly accelerating rate becoming apparent.

In a good many runs, especially at the lower iron and alkali concentrations, there existed an induction period, varying anywhere from ten to sixty minutes in length. During this time no absorption of oxygen was

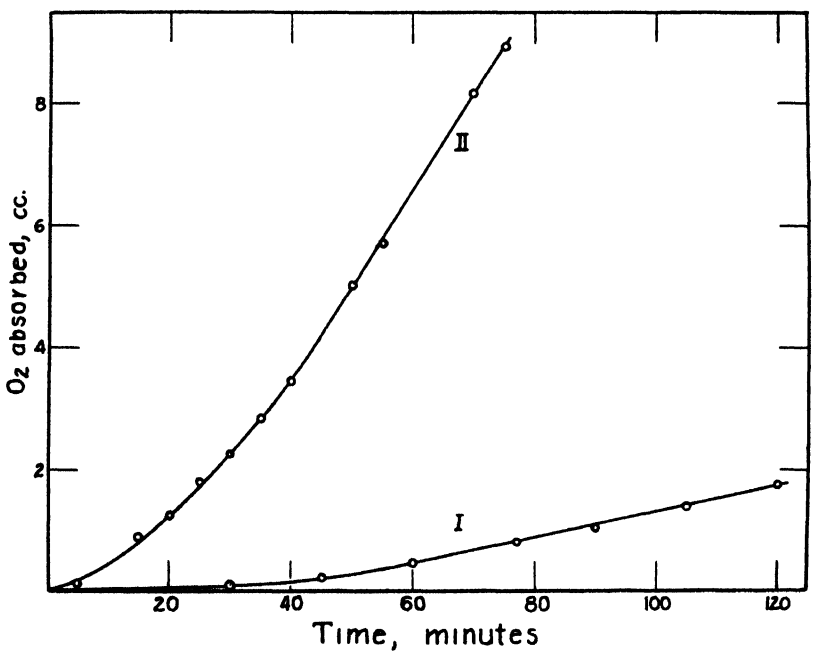

FIG. 2. TYPICAL RATE CURVE
I, The dark reaction; II, the photochemical reaction

observable. The duration of the period was not the same under any given set of conditions, and consequently duplicate runs were not exactly reproducible. However, the final constant value for the rate of reaction could be checked within about 10 per cent, and therefore in comparing oxidation rates under different conditions of concentration, etc., this constant value was used as a measure.

Runs have been made to determine the effect of concentration of mannite, of sodium hydroxide, and of ferric chloride on the rate of oxidation for the dark reaction. The data are all summarized in table 1, in which are given the initial concentrations in millimoles per cubic centimeter, the type of

apparatus in which the experiments were performed, the temperature of the reaction correct to ±0.05°C. and the reaction rate in cubic centimeters of oxygen (at N. T. P.) absorbed per minute by a 25-cc. sample of solution.

An examination of the data shows that with constant initial iron and alkali amounts, the oxidation rate is roughly proportional to the mannite concentration, up to about 0.1 molar; higher concentrations of mannite result in but a small increase in the rate. At constant iron and mannite but varying sodium hydroxide, the rates increase with the amounts of alkali added; at low alkali concentration they are less than to be expected for

TABLE 1

The dependence of rate on concentration and temperature

MANNITE	$FeCl_3$	NaOH	APPARATUS	TEMPERATURE	REACTION RATE
millimoles per cc.	*millimoles per cc*	*millimoles per cc.*		*degrees C*	*cc.* O_2 *per minute*
0.050	0 050	1.00	Bubbler	25	0.012
0.075	0 050	1.00	Bubbler	25	0.018
0.100	0 050	1.00	Bubbler	25	0 031
0.250	0.050	1.00	Bubbler	25	0.038
0.100	0.001	1 00	Bubbler	25	0.011
0.100	0 001	1.00	Shaker	25	0.012
0.100	0 003	1.00	Bubbler	25	0 014
0.100	0 010	1 00	Bubbler	25	0.022
0.100	0 010	1 00	Shaker	25	0.023
0.100	0 020	1 00	Bubbler	25	0.028
0.100	0.050	1.00	Shaker	25	0.034
0.100	0.001	1.00	Shaker	35	0.047
0.100	0.005	1 00	Shaker	35	0.112
0 100	0.010	1.00	Shaker	35	0.131
0.100	0.050	1.00	Shaker	35	0.146
0.100	0 050	0 20	Shaker	35	0.006
0.100	0.050	0.50	Shaker	35	0.064
0 100	0 050	2.10	Shaker	35	0.220

direct proportionality. This behavior very likely arises from the considerable decrease in hydroxyl ion concentration which must result with smaller initially added amounts of sodium hydroxide.

The data depicting the variation of reaction rate with added ferric chloride, other concentrations held constant, are shown graphically in figure 3. The crossed circles represent the data obtained with the shaker machine. The effectiveness of ferric salt in increasing the reaction rate falls off abov- concentrations of about 0.005 millimole per cubic centimeter. Since come paratively large amounts of ferric salt are necessary to cause even a rather

slow oxidation rate, the reaction is evidently not one in which long chains are started by a positive catalyst.

From the data given in table 1, the temperature coefficient, k_{35}/k_{25}, can be calculated at the different iron concentrations. The values vary considerably, being respectively, 4.4, 5.5, 5.4, and 4.6 for 0.001, 0.005, 0.01, and 0.05 millimoles per cubic centimeter of added ferric salt. The very high values obtained are peculiar, but their explanation is probably to be found in the temperature effect on the complex equilibria which apparently govern the oxidation.

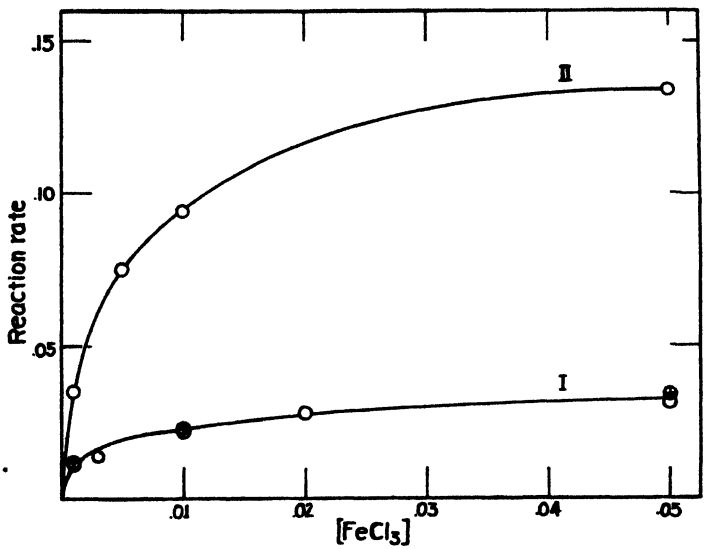

FIG. 3. THE DEPENDENCE OF REACTION RATE ON FERRIC CHLORIDE CONCENTRATION

I, the dark reaction; II, the true photochemical reaction.

Concentration rate in millimoles per cubic centimeter; reaction rate in cubic centimeters of oxygen absorbed per minute.

The photochemical reaction

The oxidation of mannitol in the presence of ferric chloride and sodium hydroxide was found to be accelerated by light. A series of photochemical experiments were carried out, using a vertical type Cooper-Hewitt mercury arc operated hot at 80 ± 1 volts and 3.0 ± 0.1 amperes as a light source. The lamp was mounted beside the reaction cell of the bubbler apparatus, but outside of the thermostat; a quartz window in the latter transmitted the light.

At the light intensity employed, the rate of the photoöxidation was increased some four or five times over the dark reaction. However, as the example plotted in figure 2 shows, the typical rate curve possessed no differ-

ent features, and therefore the reaction rate was determined as in the dark oxidation.

A series of runs were made at different iron concentrations, with sodium hydroxide and mannitol concentrations held constant. The results are recorded in table 2.

In figure 3, the true photochemical rate obtained by subtracting the dark rate from the light rate, is plotted against the added ferric salt content. The type of curve obtained is approximately that which results from increased light absorption with increased solution concentration. This is borne out by absorption spectra pictures of the solutions, which show the usual shift of absorption edge to the longer wave lengths as the concentration is raised. Thus for a layer of solution 8 mm. in depth, with mannitol and sodium hydroxide at 0.10 and 1.00 millimole per cubic centimeter, respectively, complete absorption for a ferric chloride solution of 0.001 millimole per cubic centimeter begins at about 3000 A.U. and extends

TABLE 2

The dependence of photoöxidation rate on ferric chloride concentration

NaOH, 1.00 millimole per cc.; mannitol, 0.10 millimole per cc. Arc, 80 volts, 3.0 amperes. Temperature, 25.0 ± 0.10°C.

$FeCl_3$	"LIGHT" RATE	"DARK" RATE	"TRUE LIGHT" RATE
millimoles per cc	*cc. O_2 per minute*	*cc. O_2 per minute*	*cc. O_2 per minute*
0 001	0 046	0.011	0 035
0 005	0.095	0.020	0.075
0.010	0 117	0.023	0 094
0.050	0.167	0 033	0.134

to shorter wave lengths. The absorption edge then shifts to longer wave lengths, lying at approximately 3950 A.U. and 4500 A.U., for 0.01 and 0.05 molar ferric chloride, respectively.

It may be pointed out here that the absorption pictures show clearly the formation of a ferri-mannite complex in the presence of alkali. The absorption edge lies at approximately the same point for ferric chloride alone and ferric chloride with mannitol, but on addition of sodium hydroxide, the absorption commenced at a much longer wave length. Now, although a slow rate of photoöxidation was observed for mannitol and ferric chloride in the absence of alkali, the rate was much accelerated in the presence of alkali. This suggests that the ferri-mannite complexes are chiefly responsible for the increased light absorption and the consequent increased photooxidation.

Since a test of the chain character of a reaction is given by its quantum yield, a determination of this quantity was undertaken for this photochemical oxidation. Use was made of the uranyl oxalate actinometer

described by Leighton and Forbes (12), a form of their "compound actinometer" being adapted. An auxiliary cell was placed behind the reaction cell of the bubbler apparatus. When both of these were filled with actinometer solution, they corresponded to cells 1 and 2 of Leighton and Forbes; when the reaction cell was filled with mannite–iron–alkali solution and the auxiliary cell with actinometer solution, they corresponded to cells 3 and 4. Calculation of the unknown quantum yield, ϕ', is given by

$$\phi' = \phi \frac{(m_3)}{(m_1)} \frac{(m_1 - m_2)}{(m_1 - m_4)}$$

where ϕ is the quantum yield of the uranyl oxalate photolysis, m_1, m_2, and m_4, the moles of oxalate photolyzed, and m_3 the moles of unknown reacting. Determination of the decrease in titer of cells 1 and 2 gave m_1 and m_2, and later, a determination of the amount of oxygen taken up and the decrease in titer of the auxiliary cell gave m_3 and m_4.

The absorption spectra pictures showed that for the depth of liquid obtaining in the cell, a solution with 0.01 millimole per cubic centimeter of ferric chloride (mannitol and sodium hydroxide concentrations as usual), commenced to absorb at about the same limit as the actinometer solution; consequently the quantum yield determination was made at this one concentration of ferric chloride. Also, since the operations were carried out in Pyrex vessels, the effective light must lie approximately between 3100 A. U. and 4800 A. U. For this region of the spectrum then, the average quantum yield of the actinometer photolysis was taken as 0.535. A sample calculation of the yield, molecules of oxygen reacting per quantum, is given:

Light reaction − dark reaction = True reaction
0.118 − 0.023 = 0.095 cc. O_2 per minute.

$$m_3 = \frac{0.095}{22.4} = 0.00424 \text{ millimoles } O_2 \text{ per minute.}$$

Cell 1 decreased 12.35 cc. of 0.0871 N $KMnO_4$ in 10 minutes.
m_1 = 0.0537 millimole per minute.

Cell 2 decreased 0.59 cc. of 0.0871 N $KMnO_4$ in 10 minutes.
m_2 = 0.0025 millimole per minute.

Cell 4 decreased 0.60 cc. of 0.0871 N $KMnO_4$ in 70 minutes.
m_4 = 0.0037 millimole per minute.

$$\phi' = 0.535 \frac{(0.00424)}{(0.0537)} \frac{(0.0537 - 0.0025)}{(0.0537 - 0.0004)}$$

$$\phi' = 0.040$$

An average value of 0.037 was found for the quantum yield. Thus, only one molecule of oxygen reacts for every 25 or 30 quanta of light absorbed by the solution. This low efficiency of the process shows that the oxidation does not occur by a chain mechanism.

The effect of inhibitors

The effect of small quantities of organic substance in slowing down or inhibiting a reaction also serves to indicate the chain character of a process. Such effect was sought in the present autoxidation, using known effective inhibitors of oxidation reactions (2). In no instance was any inhibition observed, as shown by the data collected in table 3. Such results are in complete accord with the quantum yield determination, and indicate more strongly the absence of chains in the oxidation process.

Hydroquinone acts as an excellent inhibitor of oxidation processes (2) under some conditions, but in the present reaction it was a marked accelerator. On the addition of freshly prepared hydroquinone solution to the ordinary reaction mixture, a very rapid up-take of oxygen occurred in the

TABLE 3

The effect of inhibitors on the oxidation rate

INHIBITOR	INHIBITOR CONCENTRATION	$FeCl_3$	TEMPERATURE	REACTION RATE
	millimoles per cc	*millimoles per cc*	*degrees C.*	*cc O_2 per minute*
Blank	—	0.01	25	0.023
Ethylamine	0 01	0 01	25	0.026
Phenol	0 01	0.01	25	0 022
Blank	—	0.05	35	0.145
Benzylamine	0.01	0.05	35	0.145
Ethylamine	0 01	0 05	35	0.148
Blank*	—	0.01	25	0.064
Ethylamine*	0 01	0.01	25	0.060

* Photochemical experiments.

first few minutes of shaking. The rate gradually fell off, to proceed eventually at a constant value which, however, was greater than ordinarily attained. Undoubtedly, in this alkaline medium the hydroquinone is itself rapidly oxidized, and in the process induces the oxidation of the mannitol.

The accelerating action of hydrogen peroxide

On the addition of hydrogen peroxide to the usual alkaline solution of mannitol and ferric chloride, the rate of absorption of oxygen by the solution was much enhanced over the usual dark rate. At the same time, the peroxide was destroyed. Thus, not only was the oxygen from the decomposing peroxide used up by the mannitol, but additional oxygen was simultaneously absorbed from the gas phase. Figure 4 shows the type of oxygen absorption–time curve obtained in the presence of peroxide; the millimoles of atmospheric oxygen absorbed are plotted against time. Also included in the figure is a plot of the millimoles of peroxide decomposed with

time. This latter curve was obtained by determining the peroxide concentration existing at the end of definite time intervals, the determinations being made by the iodometric method. Since this depends on the titration with thiosulfate of the iodine liberated from potassium iodide by the peroxide, and since the ferric iron present also liberates iodine, the proper correction for the ferric iron had to be previously determined. Blank runs on iron–peroxide mixtures showed that reasonably reliable results could be obtained in this manner.

More extended runs with peroxide present showed that after twenty-five to thirty minutes of shaking the oxidation rate slowed down to continue at a constant value. This rate was about 70 per cent faster than the final

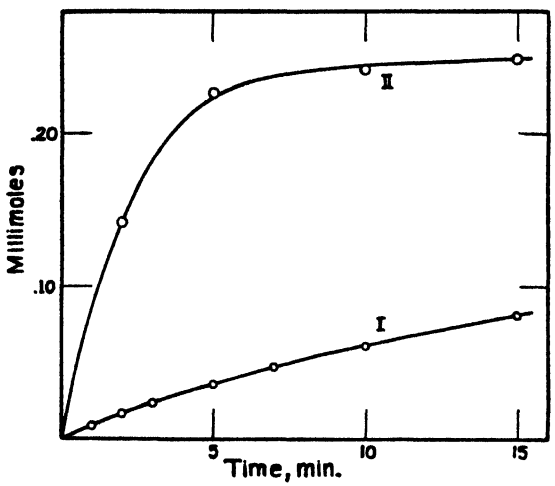

FIG. 4. RATE CURVES FOR THE OXIDATION ACCELERATED BY HYDROGEN PEROXIDE
I, millimoles of oxygen absorbed; II, millimoles of hydrogen peroxide decomposed

value attained in the dark under the usual conditions without peroxide. Furthermore, qualitative tests showed that no peroxide existed at the end of such runs.

The initial rates of oxygen up-take in the presence of peroxide depended on the concentration of ferric chloride, as did the final rates attained after the peroxide had all disappeared. For both these rates, the plot of the dependence of rate on ferric salt concentration gave a curve of practically the same form as shown in figure 3 for the unaccelerated autoxidation. With no ferric chloride present, however, oxygen was evolved, although not quantitatively. The initial rate of oxidation was also shown to be dependent on the initial peroxide concentration, and an approximate temperature coefficient determination gave a value of 2.6 for k_{35}/k_{25}.

DISCUSSION

The experimental evidence on the oxidation of mannitol in the presence of alkali and ferric salt indicates clearly that the oxidation is not a chain reaction. The low quantum yield, the absence of inhibitory effect by added organic substances, and the evidence that the ferric salt does not function as a trace catalyst, all point to the fact that a chain process is not operative.

As to the actual mechanism of the autoxidation, but little can be said since the data are not readily amenable to kinetic treatment. The auto-accelerating type of rate curve observed cannot result from preliminary oxidation of impurities acting as inhibitors, for such an explanation holds only in event of a chain process. The auto-acceleration is explicable, however, on the assumption that products are formed during the oxidation which themselves are more easily oxidized than the original substance. On the other hand, Spoehr (17, 18) has demonstrated that glucose, and mannitol also, in the absence of oxygen were capable of reducing his sodium ferripyrophosphate catalyst to the ferrous compound, and he considered that the induction period found in the reduction reaction accounted for the induction period of the oxidation.

The dependence of the reaction rate on iron salt concentration in the manner shown in figure 3 would suggest that the oxidation process is very complicated and that complex equilibria regulate the speed of reaction. Certainly these data show definitely that the concentration of ferri-mannite complexes is not the rate controlling factor, since their concentration must be very nearly directly proportional to the amount of ferric salt initially added.

The acceleration of the oxidation by hydrogen peroxide may furnish evidence of some importance. Haber and Willstätter (9) have proposed a chain mechanism for the enzymotic oxidation of alcohols and aldehydes. They have suggested that free hydroxyl radicals served as active links in the chain, operating to produce organic radicals which were then oxidized by atmospheric oxygen. Now, the decomposition of hydrogen peroxide supposedly proceeds through a chain also involving hydroxyl radicals, and Haber and Weiss (8) have recently indicated how the chain can be started in catalytic peroxide decomposition by iron salt. Consequently, in the presence of a high concentration of hydroxyl chain propagators furnished by decomposing hydrogen peroxide, an alcohol might be expected to show increased up-take of oxygen from the gas phase. Taylor and Gould (21) have demonstrated that such is the case for the interaction of ethyl alcohol and oxygen in the presence of photodissociated peroxide. Figure 4 amply demonstrates a parallel behavior for mannitol and thermally decomposed peroxide. Now, the evidence on the autoxidation of mannitol in the presence of iron and alkali indicates that any chain theory for the oxidation

of polyalcohols at least is untenable. Furthermore, whereas the Haber-Willstätter chain theory would require the up-take of at least one oxygen molecule for every hydrogen peroxide molecule decomposed, a comparison of the rates of peroxide decomposition and oxygen absorption given in figure 4 shows that initially about eight peroxide molecules decompose for every one of oxygen absorbed; only when nearly all the peroxide has disappeared is a one to one ratio approached. Thus, although a chain process for the oxidation cannot be presumed, some sort of an oxidation mechanism involving free radicals may be operative in both the accelerated and the normal oxidation. Qualitative evidence obtained from the fact that hydroquinone is an activator lends support to this view, because the oxidation of such a substance falls into the Haber-Willstätter scheme. In the present instance, the hydroquinone can operate as an accelerator by supplying an increased concentration of hydroxyl.

Turning to the deterioration of cellulose, the close parallelism which exists between the oxidation of alkali-cellulose and of alkaline mannitol solutions by atmospheric oxygen is brought out by a comparison of the experimental results reported by Davidson (6) and those presented above. The same auto-accelerating type of curve is obtained for both oxidation processes, and the dependence of the oxidation rate on iron concentration is very similar. Since the oxidation of mannitol in the presence of iron and alkali is not a chain process, this suggests that the oxidation of cellulose or alkali-cellulose does not involve a chain. Attempts to prevent the deterioration of cellulose by addition of inhibitors, which works so effectively in the retardation of the aging of rubber for example, would most probably be ineffective with cellulose. Methods which involve removing positive catalysts or the prevention of any catalytic activity by such would be more likely to yield desirable results.

Certain empirical observations are closely analogous to the acceleration of oxygen up-take caused by hydrogen peroxide in the oxidation of the alkaline mannite–iron mixtures. It is well-known, of course, that fabrics are tendered in peroxide or chlorite bleach liquors, the more rapidly if first impregnated with heavy metal (10). Likewise, the aging of alkali-cellulose is accelerated manyfold by the addition of small quantities of iron and peroxide (27). Chemical evidence cited by Kauffmann (11) indicates that in the decomposition of chlorite bleaches and in the accompanying dye bleaching, a chain mechanism might operate. Thus in the presence of activators, notably hydrogen peroxide, the chlorite bleach showed a much increased oxidation activity for dyes and other substrates such as cellulose. Presumably the peroxide served to maintain a high concentration of the chain carrier, the hydroxyl radical. However, the evidence presented in the case of the mannitol oxidation accelerated by peroxide would indicate that the oxidation of a comparable substrate such as cellulose would not be

a chain process, although it could be considerably accelerated by the presence of the peroxide.

SUMMARY

1. The effect of inorganic substances, ferric chloride and sodium hydroxide, on the autoxidation of mannitol has been investigated for both the dark and the photochemical oxidations.

2. The oxidation is auto-accelerating in nature.

3. The oxidation is not a chain process. This is shown by the low quantum yield of the photo-reaction, and by the absence of any inhibition by known effective oxidation inhibitors.

4. A considerable acceleration of the rate of absorption of oxygen from the gas phase by mannitol solutions is produced by thermally decomposing hydrogen peroxide.

5. The application of the results obtained in the autoxidation of mannitol to problems of oxidation of related substances, particularly to the deterioration of cellulose and to bleaching processes, is indicated.

The author wishes to express his sincere thanks to Professor Hugh S. Taylor, who suggested this line of work, and who served for the Textile Foundation as director of the research. Without his continued aid and interest the problem could not have been carried through to its present stage of development.

Grateful acknowledgment is made to the Textile Foundation for the fellowship under which this work was carried out.

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THE OXIDATION OF MANNITOL BY OXYGEN PHOTOSENSITIZED BY HYDROGEN PEROXIDE

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In a previous paper (3) on the autoxidation of mannitol in the presence of ferric chloride and sodium hydroxide, evidence was presented to show that the oxidation was not a chain process. The importance of this finding to problems of oxidation of related substances, particularly in connection with the deterioration of cellulose, was indicated. Furthermore, its bearing on the Haber-Willstätter (2) chain theory of alcohol and aldehyde oxidation was emphasized. It was pointed out that, although in the case of polyalcohols a chain theory was unnecessary, experiments in which the rate of oxygen up-take was markedly accelerated by thermally decomposing hydrogen peroxide suggested that a mechanism of the Haber-Willstätter type might be applicable.

Taylor and Gould (4) have recently shown that ethyl alcohol interacts with gaseous oxygen when photosensitized by hydrogen peroxide. The induction of oxidation in this manner is convenient and efficient, as compared with methods involving thermal peroxide decomposition, and should yield results of a quantitative nature.

For their particular oxidation, Taylor and Gould established the existence of short chains, and concluded that the experimental results were compatible with the ideas of Haber and Willstätter. The photosensitization may be formulated in the following manner:

$$H_2O_2 + h\nu = 2OH \qquad \text{(a)}$$

$$OH + RCH_2OH = R\overset{/}{C}H(OH) + H_2O \qquad \text{(b)}$$

$$RCH_2OH + R\overset{/}{C}H(OH) + O_2 = 2RCHO + OH + H_2O \qquad \text{(c)}$$

On the basis of the above scheme, each hydrogen peroxide molecule decomposed by light should cause the absorption of not less than two oxygen molecules. Many more will react if a long chain follows the initial step. A comparison of the simultaneous rates of peroxide decomposition and

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oxygen absorption therefore should give some idea as to the chain length involved in the reaction. Only at the higher concentrations of the alcohol will approach be made to the true chain length, as then the probability is greatest that each hydroxyl radical will start an oxidation step. In such a range, the observed reaction rates should be independent of the alcohol concentration. With these considerations in mind, an examination of the oxidation of aqueous mannitol solutions photosensitized by hydrogen peroxide has been made over a range of both peroxide and mannitol concentration.

EXPERIMENTAL

The shaking machine used previously in the autoxidation of mannitol, and also used by Taylor and Gould, was employed in these experiments. A quartz reaction vessel was available, and a quartz window was fitted in the thermostat in which the shaker device carrying the reaction vessel was immersed. The thermostat was regulated at 25°C. ± 0.05°C. Two vertical type Cooper-Hewitt mercury arcs placed side by side in front of the quartz window served as the source of light. They were each operated at 70 ± 1 volts and 4.0 ± 0.1 amperes.

The mannitol solutions were made up by accurately weighing out samples of a recrystallized Eastman product and dissolving in the required amounts of distilled water. The hydrogen peroxide solutions were obtained by diluting Merck's Superoxol to the desired concentrations.

In carrying out a run, the general procedure was to fill the apparatus with oxygen, and then introduce the solutions from calibrated pipettes. The added solutions were of such concentrations that the sample in the reaction vessel possessed the concentrations desired for the particular experiment, and also totaled 25 cc. in final volume in all cases. After a 10-minute period of shaking in the dark, the reaction was initiated by removing a shutter from before the window. Runs of ten minutes in length were made in most cases. The rate of oxygen absorption was followed by observing the decrease in oxygen volume at constant pressure.

At the end of the run, determination of the acid produced was made by titration of the total contents of the reaction vessel with 0.1 N sodium hydroxide with phenolphthalein indicator. This titration was carried out as rapidly as possible, and the hydrogen peroxide was then determined by the iodometric method. Appropriate control analyses were made in all cases.

RESULTS

Preliminary experiments showed that on illumination with a mercury arc, an aqueous solution of mannitol and hydrogen peroxide absorbed oxygen from the gas phase. No reaction whatever was observed when the

mixture was shaken in the dark for periods of ten to thirty minutes, and, also, no oxygen absorption persisted in the dark after cutting off the light. Mannitol alone did not take up observable amounts of oxygen when rayed ten to thirty minutes under existing conditions. Such behavior is to be expected from the fact that absorption spectra pictures of aqueous mannitol solutions indicated that even weak absorption did not take place for light of wave length longer than about 2300 A.U.

A series of runs was made to determine the variation of both the oxygen absorption and the peroxide decomposition with change in mannitol concentration. This was done for each of three initial peroxide concentrations. Also, the rate of photolysis of pure aqueous hydrogen peroxide solutions was followed by measuring the production of oxygen. This was possible because the apparatus is equally well adapted for observing oxygen absorption or evolution.

Hydrogen peroxide photolysis

In a given experiment, the rate of photolysis of pure aqueous hydrogen peroxide solutions did not quite follow the equation of a first order reaction. When approximately 50 per cent of the peroxide had disappeared, the calculated constant had drifted to a value about 20 per cent greater than the initial. The decomposition rate was thus not exactly directly proportional to the initial peroxide concentration.

The value chosen for the rate of peroxide photolysis was that given by the oxygen evolution (at N. T. P.) observed during the first two minutes, at the end of which time the concentration was still about 85 per cent of the original. The rate so obtained was expressed in millimoles of peroxide decomposed per minute for 25 cc. of solution. In view of the fact that duplicate runs agreed only within 15 per cent, this method of choosing the initial rate of reaction provided a value within the limit of accuracy of the experiments.

Photosensitized mannitol oxidation

For a typical experiment in which oxygen was taken up by an illuminated mannitol-peroxide mixture, a plot of the cubic centimeters of oxygen absorbed against time gave an exact straight line. Although most of the individual experiments were but ten minutes long, tests indicated that this linear relationship extended for thirty minutes or more in almost every case. The slope of the straight line obtained from the graph was taken as the rate of reaction, and expressed as cubic centimeters (at N. T. P.) of oxygen absorbed per minute for a 25-cc. sample.

The rate of photodecomposition of hydrogen peroxide in the presence of mannitol was obtained simply by determining the amount disappearing in a 10-minute run, dividing this by ten, and expressing the result as milli-

moles of peroxide decomposed per minute. This procedure is justified by the fact that in every case, the peroxide concentration at the end of ten minutes was still over 78 per cent of the initial, so the rate can be taken essentially as linear for such a period. In fact, determinations at the

TABLE 1

The dependence of reaction rate on concentration

HYDROGEN PEROXIDE	MANNITOL	I/I_0	RATE OF REACTION				RATIO OF RATE OF O_2 ABSORBED TO H_2O_2 DECOMPOSED
			O_2 absorption		H_2O_2 decomposition	Acid formation	
millimoles per cc.	*millimoles per cc.*		*cc per minute*	*millimoles per minute*	*millimoles per minute*	*millimoles per minute*	
0.0110	0 0	1.09	0 250*	0.0114*	0.0227	—	—
0.0110	0 001	1 09	0 052	0 0023	0 0059	0 0043	0 4
0 0110	0 005	1 09	0 082	0 0037	0 0044	0 0037	0 8
0 0110	0 010	1 09	0.092	0 0041	0 0042	0 0034	1 0
0.0110	0 10	1 09	0 111	0 0049	0 0025	0 0021	1 9
0 0108	0 10	1 09	0 110	0 0049	0 0021	0 0024	2 2
0.0256	0 00	1 07	0 500*	0.0223*	0 0447	—	—
0.0269	0.00	1 07	—	—	0.0410	—	—
0 0266	0.001	1 07	0.042	0.0019	0 0120	0 0068	0 1
0.0271	0 005	1 07	0 141	0 0063	0 0096	0.0071	0 7
0.0266	0 010	1.07	0 162	0.0072	0 0075	0.0064	1 0
0.0271	0 050	1.07	0 208	0.0093	0 0052	0 0054	1.8
0.0266	0 10	1.07	0.208	0 0093	0 0050	0 0053	1 9
0 0271	0 10	1 07	0.208	0 0093	0.0045	0 0051	2 0
0 0522	0 00	1 00	—	—	0 0974	—	—
0 0529	0 00	1 00	1 015*	0 0453*	0 0907	—	—
0.0525	0 001	1 00	0.125*	0 0055*	0.0234	0 0076	—
0.0514	0 005	1.00	0.151	0.0067	0.0166	0.0127	0 4
0.0527	0 010	1 00	0 213	0 0095	0.0154	0 0117	0.6
0.0515	0 050	1 00	0 293	0.0131	0 0100	0 0094	1 3
0.0496	0 10	1 09	0.298	0 0133	0.0087	0 0084	1 5
0 0521	0 10	1 07	0 302	0 0135	0 0088	0 0086	1.5
0 0527	0 10	1 00	0 302	0 0135	0.0095	0.0089	1.6
0.0518	0.10	1.00	0 296	0 0132	0.0082	0 0087	1.6

* In these experiments, oxygen was evolved at this rate.

higher mannitol concentrations showed that this linear behavior held over a period as long as thirty minutes.

The rate of formation of acid was also taken as linear for a 10-minute period. The amount resulting in that time was ascertained and the rate was determined as millimoles formed per minute. In longer runs the acid was produced in amounts greater than a linear rate would provide.

The reproducibility of the rates of oxygen up-take was good, check runs agreeing within 2 to 3 per cent. The rates of peroxide decomposition and acid formation were not so readily checked, however, variations of 10 per cent occurring between duplicates.

In order to check the light intensity for each series of runs at a given peroxide concentration, a reference run was always made under the standard conditions of 0.052 millimole per cubic centimeter of peroxide and 0.10 millimole per cubic centimeter of mannitol. The runs of the several series could then be related. Variations in the light intensity amounted to no more than 10 per cent.

The rates of reaction as determined according to the methods outlined above are recorded in table 1, and the other pertinent data are also given. (The figures in the column I/I_0 are the factors obtained from the reference runs made to check the light intensity. The rates actually observed have been divided by these factors, and the quotients so obtained are the values recorded in the table as rates of reaction.)

DISCUSSION

Examination of the data of the table indicates that at a constant initial peroxide concentration, variation of the mannitol concentration causes an increase in the rate of absorption of oxygen and a simultaneous decrease in the rate of decomposition of peroxide. As a case in point, the data obtained with a peroxide concentration of 0.027 millimole per cubic centimeter are plotted in figure 1. This graph shows the dependence of both the oxygen absorption rate and the peroxide decomposition rate, respectively, on the initial mannite concentration. At zero mannite content, oxygen is evolved in amount equivalent to the peroxide decomposed; then, at comparatively low mannitol concentrations, oxygen absorption commences while peroxide destruction is inhibited. In some cases, as much as eight- or nine-fold inhibition is observed. The graph also makes apparent the important fact that at sufficiently high mannite concentrations the rates of both the peroxide decomposition and oxygen absorption are independent of the mannite concentration.

This behavior is practically repeated with the two other peroxide concentrations used. Taking the values obtained with the mannite concentration of 0.10 millimole per cubic centimeter, a plot is made in figure 2 of the dependence of the oxygen absorption rate and the peroxide decomposition rate on the initial peroxide content. The rate of disappearance of peroxide appears as directly proportional to the amount of peroxide initially present. The same is not true, however, for the rate of oxygen absorption, as the oxygen up-take at the higher peroxide concentrations is less than that necessary for direct proportionality. Such conduct can be explained on the basis that at sufficiently high peroxide content the perox-

ide is not completely efficient in sensitizing the oxidation. Some of the peroxide may be decomposed with evolution of oxygen, thereby causing an apparently slower rate of oxygen up-take.

Emphasis has been laid on the important fact that at sufficiently high mannite content, the rates of peroxide decomposition and oxygen absorption become independent of the mannitol concentration. As pointed out in the introductory paragraphs, the existence of such a range suggests that

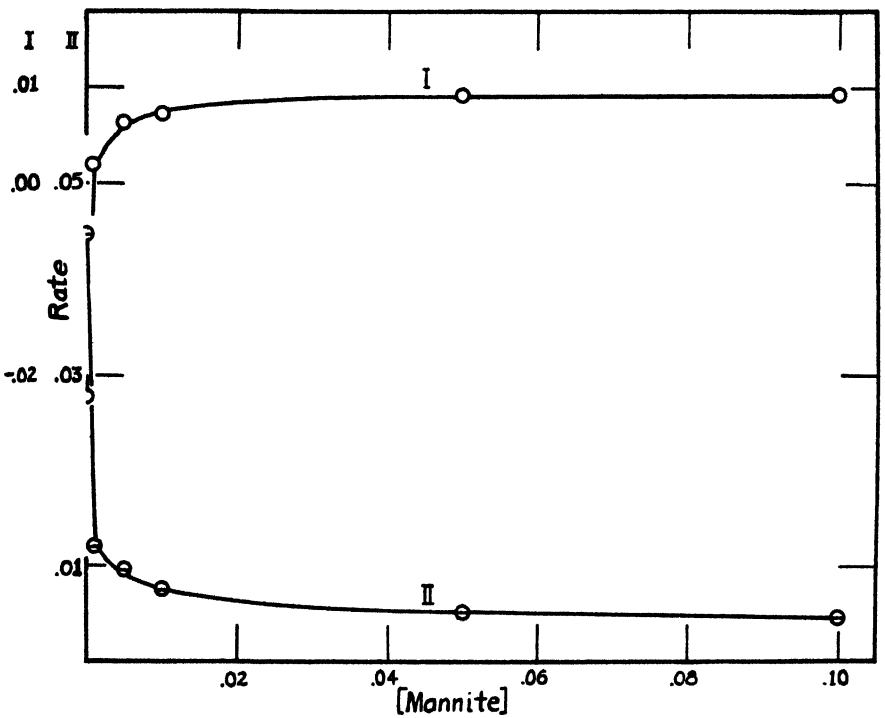

FIG. 1. THE DEPENDENCE OF REACTION RATE ON MANNITE CONCENTRATION

Concentration in millimoles per cubic centimeter; reaction rates in millimoles per minute.

I. Oxygen absorption. The negative coördinates indicate oxygen evolution.

II. Hydrogen peroxide decomposition.

very nearly every photodecomposed peroxide molecule starts off an oxidation process, and therefore comparison of the two rates of reaction obtaining in this region of mannite concentration should serve as a measure of the chain length. The figures for the ratio of the rates of oxygen absorption to peroxide decomposition have been calculated over the whole range and are recorded in table 1. These bring out the fact that a maximum of two oxygen molecules is absorbed for each peroxide molecule decomposed, this maximum being attained under the most favorable conditions.

The optimum ratio of two oxygen molecules absorbed for each peroxide molecule decomposed indicates that chains are not set up in the oxidation process. On the accepted basis (5) that photodissociation of a peroxide molecule results in two hydroxyl radicals, each hydroxyl must induce the absorption of but one oxygen molecule. The scheme previously given in the introduction would indicate at least a one to one ratio of hydroxyl produced to oxygen absorbed, and suggests that a much higher ratio is possible. The magnitude of the ratio will depend, of course, on the relative efficiencies

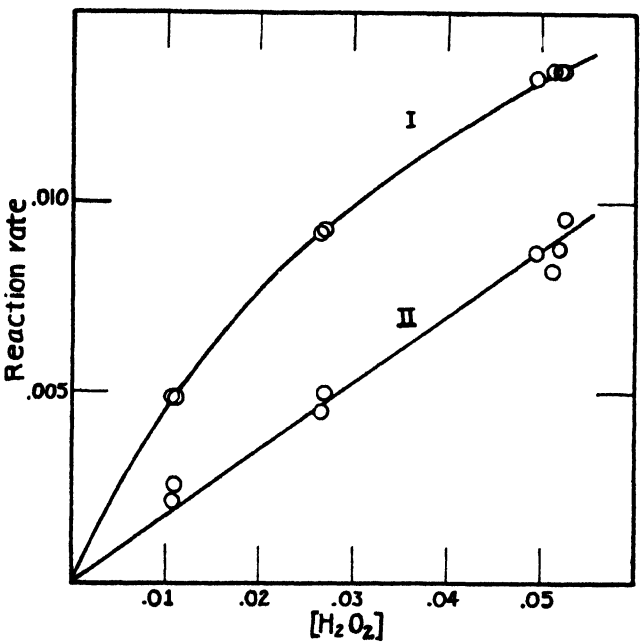

FIG. 2. THE DEPENDENCE OF REACTION RATE ON HYDROGEN PEROXIDE CONCENTRATION

Concentration in millimoles per cubic centimeter; reaction rates in millimoles per minute.

I. Oxygen absorption. II. Hydrogen peroxide decomposition.

of the chain propagating process to the various possible chain breaking reactions, and low ratios are not impossible. Therefore, although the evidence indicates that for the oxidation of polyalcohols a chain mechanism is unnecessary, the original scheme for the photosensitization cannot be excluded. The fact that photodissociation of peroxide causes absorption of oxygen is explicable on a mechanism of the Haber-Willstätter type involving hydroxyl.

The formation of acid during the oxidation of the mannitol occurs in a reasonable manner. At the low mannite concentrations, very nearly all

of the oxygen and peroxide used up appears as acid formed. Furthermore, the indications are that oxidation of both primary alcohol groups of the mannite molecule takes place, for slightly less than two moles of acid are formed for each mole of polyalcohol originally present. In the high mannitol concentration range, the amount of oxygen used up cannot be accounted for quantitatively as acid. Only partial oxidation to an aldehyde stage must occur in such cases. This is to be expected, as the concentration relationships favor the probability of oxidation of a new polyalcohol molecule rather than of one already partially oxidized. However, the fact that some acid is formed, as well as the observations at low mannite concentration, indicate that the specific oxidation rate of the first reaction product is greater than that of the mannitol itself.

The fact that oxidation proceeds to an acid does not affect in any way the conclusion drawn concerning the chain length in the reaction. The aldehyde oxidation to the acid stage was supposed by Haber and Willstätter to proceed in the same manner as the alcohol oxidation, and the important point is that each peroxide molecule induces the absorption of only two oxygen molecules, whether these go to oxidize aldehyde or alcohol.

Several runs were made in an attempt to determine the effect of an inhibitor on the photosensitized oxygen absorption. Ethylamine was the only substance tried; it has been shown to be a very efficient inhibitor for the photolysis of peroxide (1) and at the same time exhibits no "internal light filter" effects. Experiments were performed with hydrogen peroxide and mannitol concentrations of 0.052 and 0.10 millimole per cubic centimeter, respectively.

At an ethylamine concentration of 0.01 millimole per cubic centimeter, the oxygen absorption rate was decreased, for example, from the normal value of 0.302 cc. per minute to 0.254 cc. per minute; at the same time the peroxide decomposition rate was increased from 0.0092 millimole per minute to 0.180 millimole per minute. These figures represent a 16 per cent decrease and almost a 100 per cent increase, respectively. Similar results, but of lesser magnitude, were obtained at an ethylamine concentration of about 0.002 millimole per cubic centimeter.

The reason for the acceleration in the peroxide decomposition rate is not clear. The fact is known that ethylamine increases the thermal decomposition, probably because the solution is rendered alkaline, and a similar effect may enter here. In any event, this acceleration does not result in efficient sensitization of the mannitol to oxygen absorption. In fact, destruction of the peroxide with partial evolution of oxygen must occur, rendering an apparently slower oxygen absorption rate. These effects with ethylamine as an inhibitor do not, therefore, influence the previous result, namely, that reaction chains are not present in the oxidation.

SUMMARY

1. The oxidation of aqueous mannitol solutions by oxygen, photosensitized by hydrogen peroxide, has been investigated over a range of mannitol and peroxide concentrations.

2. At sufficiently high mannite concentrations, the rates of both the oxygen absorption and peroxide decomposition become independent of the mannite concentration.

3. In such a concentration range, but two oxygen molecules are absorbed by the mannitol solution for each peroxide molecule disappearing.

4. It follows that the photosensitized oxidation is not a chain process.

5. The bearing of the observations on the Haber-Willstätter theory of alcohol and aldehyde oxidation is discussed.

The author wishes to express his sincere thanks to Professor Hugh S. Taylor for his assistance and interest during this work.

Grateful acknowledgment is made to the Textile Foundation for the fellowship under which this research was carried out.

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II. THE ADSORPTION OF CALCIUM AND COPPER FROM AMMONIACAL MEDIUM BY SILICA GEL[1]

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A detailed study has been made of the adsorption of calcium hydroxide alone and of copper hydroxide and of calcium hydroxide in the presence of ammonia and ammonium salts by silica gel with the purpose of finding out in what forms the cations are held at the surface of the gel.

The gel used and the general procedure followed are described in previous communications (5, 6).

ANALYTICAL

The amount adsorbed was determined by analysis of the supernatant liquid and of the solution obtained after extraction of the washed gel with a known volume of standard acid. Calcium was determined by the oxalate procedure, ammonia in the absence of copper volumetrically by oxidation with calcium hypochlorite, and copper iodometrically. It was found that ammoniacal copper solutions on standing give rise to the formation of nitrite, which interferes badly with the volumetric determination. The interference was eliminated by removing the nitrite by evaporation with sulfuric acid. If the presence of nitrite is ignored, deviating results may be obtained from the direct iodometric analysis. A solution originally 0.0522 molar in copper, 0.02 molar in ammonium chloride, and 1.1 molar in ammonia gave an iodometric titer of 0.0522 after three days, 0.0538 after seven days, 0.0568 after twelve days, 0.0588 after nineteen days. After seven months the results of the titration were inconsistent, but at least 20 per cent high.

ADSORPTION OF CALCIUM HYDROXIDE

Although the solubility of the silica gel in calcium hydroxide solutions was very small, no adsorption equilibrium could be attained even after long periods of shaking. This is clearly shown by the curves in figures 1 and 2.

In the former case 0.5 g. of gel and in the latter 0.2 g. of gel was shaken

[1] From a thesis submitted by Vernon A. Stenger, J. T. Baker Fellow in Analytical Chemistry, 1932–1933, to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1933.

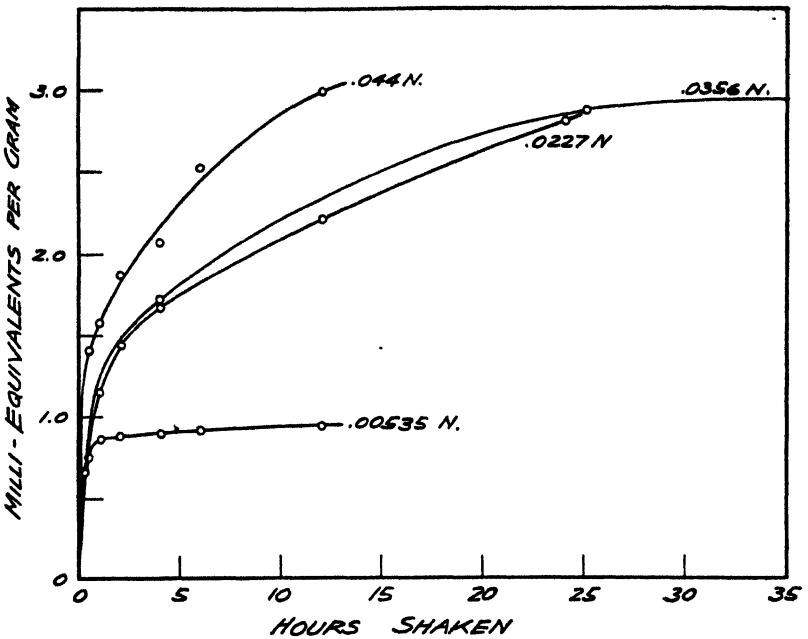

FIG. 1. TIME EFFECT. ADSORPTION OF CALCIUM HYDROXIDE

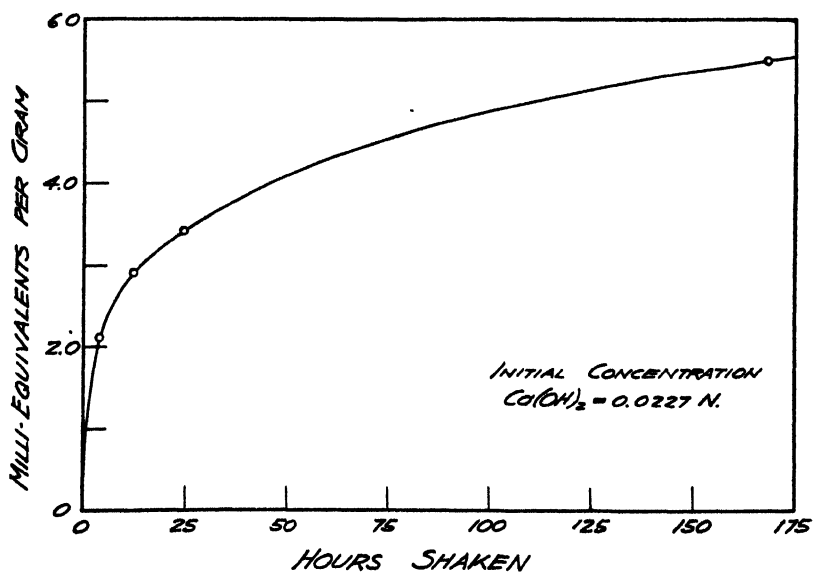

FIG. 2. TIME EFFECT. ADSORPTION OF CALCIUM HYDROXIDE

with 100 cc. of solution. The calcium hydroxide is strongly adsorbed by the gel; however, since the calcium silicate formed is insoluble, the adsorbed base obstructs the capillaries and inhibits or prevents the diffusion of more base into the interior of the gel.

In order to compare the adsorption of calcium hydroxide with that of alkali hydroxides, experiments were made in which 0.5 g. of gel was shaken for four hours with hydroxide solutions. The results are plotted in figure 3 of the previous paper (6) and given here in table 1.

MIXTURES OF CALCIUM HYDROXIDE AND AMMONIA

The adsorption of calcium and ammonium hydroxides was determined after various periods of shaking. Even after seven days of continuous shaking, no adsorption equilibrium was attained, as can be seen from the curves in figures 3 and 4.

TABLE 1

Adsorption of calcium hydroxide

0.5 g. of gel; 4 hours of shaking

CONCENTRATION OF $Ca(OH)_2$		GEL DISSOLVED	$Ca(OH)_2$ ADSORBED	
Initial	Final		Analysis solution	Analysis extract
N	*N*	*per cent*	*milliequiv per gram*	*milliequiv per gram*
0.00535	0.0012	4 07	0 87	0 93
0 0111	0 0033	4 34	1 64	1.64
0.0221	0 0138	0 86	1 68	1 69
0.0227*	0 0186	2 66	2 10	2 12
0.0356	0 0271	1 16	1.72	1 71
0.0443	0 0339	1 47	2 10	2 03

* 0 2 g. of gel used.

The points of the curves in figure 3 were obtained by shaking 0.5 g. of gel with 100 cc. of 0.022 *N* calcium hydroxide in 0.0375 *N* and in 0.75 *N* ammonia, respectively. The points in figure 4 were obtained by shaking 0.2 g. of gel with the same solutions. The molar ratio of ammonia to calcium hydroxide adsorbed decreases with the time of shaking. For comparison with the adsorption of the ammino copper complex, it is of interest to report some results. This is done in table 2.

The adsorption of calcium hydroxide, or more probably its speed of adsorption, increases with increasing concentrations of ammonia in the solution. A maximum is reached in about 0.3 *N* ammonia, and with increasing concentration of the latter, the adsorption of calcium hydroxide decreases (see figure 5). This is easily seen from some results reported in table 3 after a shaking period of four hours.

In order to be able to compare the adsorption of calcium with that of copper from ammoniacal medium, experiments have been made with

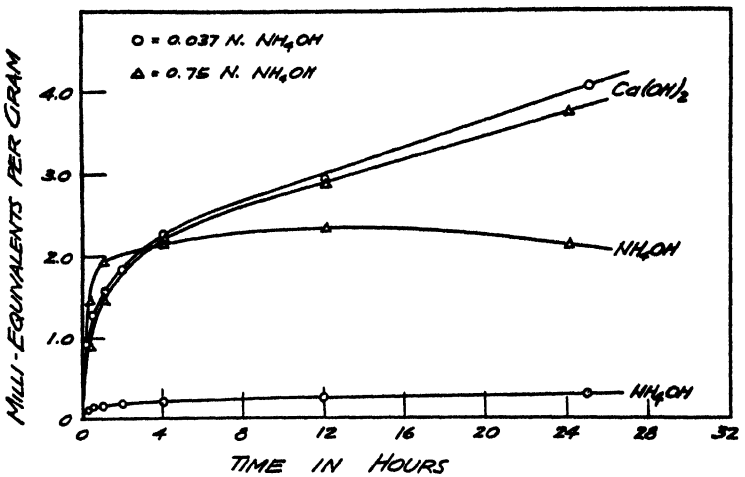

FIG. 3. TIME EFFECT. ADSORPTION FROM CALCIUM HYDROXIDE–AMMONIUM HYDROXIDE MIXTURES

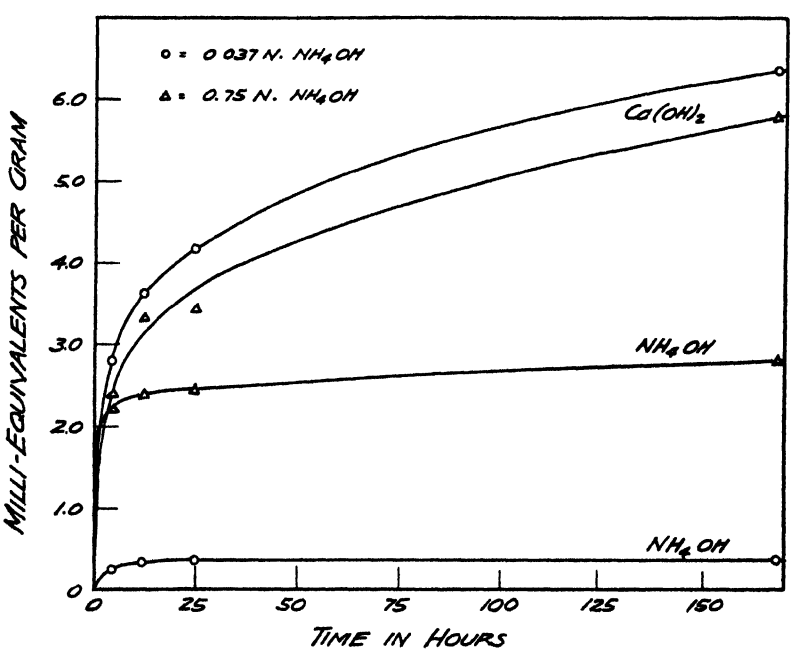

FIG. 4. TIME EFFECT. ADSORPTION FROM CALCIUM HYDROXIDE–AMMONIUM HYDROXIDE MIXTURES

TABLE 2

Adsorption of calcium hydroxide and ammonia (time-adsorption)

0.2 g. of gel; concentration of $Ca(OH)_2$, 0.0227 *N*

TIME OF SHAKING	FINAL NORMALITY		GEL DISSOLVED	BASE ADSORBED MILLIEQUIVALENTS PER GRAM			MOLAR RATIO NH_3/$Ca(OH)_2$ ADSORBED
	$Ca(OH)_2$	NH_4OH		Total base	$Ca(OH)_2$	NH_3	
Initial concentration of NH_3 = 0.037 *N*							
hours	*N*	*N*	*per cent*				
4	0 0172	0 0368	2 5	3 08	2 81	0 27	0 19
12	0 0156	0 0366	3 1	3 97	3 63	0 34	0 19
24	0 0146	0 0364	3 3	4 53	4 17	0 36	0 17
168	0 0102	0 0364	4 7	6 75	6 37	0 38	0 12
Initial concentration of NH_3 = 0.75 *N*							
4	0 0178	—	2.3	4 63	2 41	2 22	1 84
12	0 0163	—	2 8	5 72	3 32	2 40	1 45
24	0 0158	—	2 8	5 87	3 45	2 42	1 40
168	0 0114	—	4 9	8 66	5 83	2 83	0 97

TABLE 3

Adsorption of calcium hydroxide and ammonia (influence of concentration of ammonia

0.5 g. of gel; 100 cc. of solution; 4 hours of shaking

INITIAL NORMALITY		FINAL NORMALITY		GEL DISSOLVED	BASE ADSORBED MILLIEQUIVALENTS PER GRAM			MOLAR RATIO NH_3/$Ca(OH)_2$ ADSORBED
$Ca(OH)_2$	NH_3	$Ca(OH)_2$	NH_3		Total	$Ca(OH)_2$	NH_3	
N	*N*	*N*	*N*	*per cent*				
0 0111	0	0 0033	0	4 3	1 64	1 64	—	—
0 0109	0 0185	0 0023	0 0179	5 6	1 97	1 80	0 17	0 19
0 0109	0.0376	0 0018	0 0363	5 7	2 24	1 94	0 30	0 31
0 0221	0	0.0138	0	0 9	1 69	1 69	—	—
0 0222	0.0183	0.0119	0 0178	1 3	2 19	2 05	0 14	0 14
0 0222	0.0374	0.0108	0 0365	1 1	2 52	2 28	0 24	0 21
0 0217	0 0750	0.0086	0 0731	1 0	3 06	2 62	0 44	0 34
0 0180	0.250	0 0030	0 25	2 3	4 06	3 01	1 05	0.70
0.0180	0 50	0 0038	0 50	2 0	4 48	2 86	1 62	1.1
0.0180	1.00	0 0066	1 0	1 1	4 65	2 25	2 40	2 1

mixtures of calcium chloride and ammonia, some in the presence of ammonium chloride. The results are given in table 4.

The tremendous inhibiting effect of the excess of ammonium salt upon the adsorption of calcium hydroxide is clearly demonstrated by the curves in figure 6.

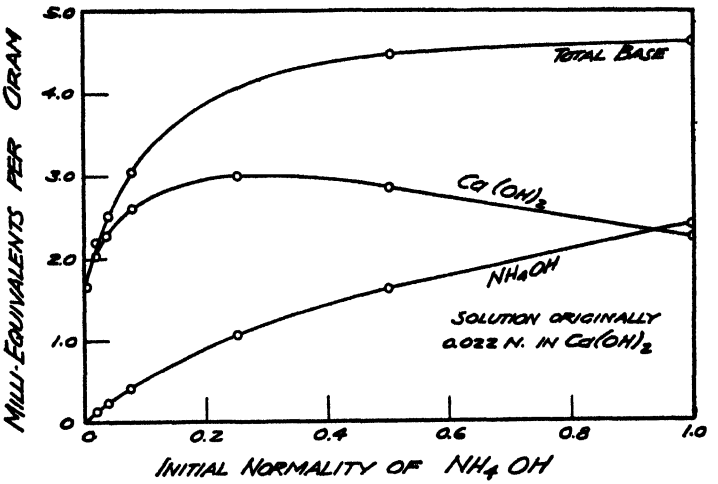

FIG. 5. FOUR-HOUR ADSORPTION FROM AMMONIUM HYDROXIDE–CALCIUM HYDROXIDE SOLUTIONS

TABLE 4

Adsorption of calcium hydroxide and ammonia from mixtures of 0.0229 N calcium chloride, ammonia, and ammonium chloride

0.2 g. of gel and 100 cc. of solution

TIME SHAKEN	FINAL NORMALITY		GEL DISSOLVED	BASE ADSORBED MILLIEQUIVALENTS PER GRAM			MOLAR RATIO NH_3/$Ca(OH)_2$ ADSORBED
	Ca	NH_3		Total	$Ca(OH)_2$	NH_3	
Concentration of NH_3 = 0.0373 *N*							
hours	*N*	*N*	*per cent*				
4	0.0189	0.0335	9.1	2 61	2.27	0.34	0.30
12	0.0175	0.0315	12 1	3 46	3 10	0.36	0.23
24	0.0175	0 0312	11.7	3.57	3 21	0.36	0.22
168	0.0161	0 0298	11.8	4.36	3 97	0 39	0.20
Concentration of NH_3 = 0.75 *N*							
4	0 0173		5 3	5.06	3.07	1.99	1.30
24	0.0155		6 5	6 26	4.07	2.19	1.08
335	0 0139		9 0	8.31	4.99	3.32	1.33
Concentration of NH_3 = 0.75 *N*; of NH_4Cl = 0.75 *N*							
4	0.0220		10.1	3.04	0.63	2.41	7.65
12	0.0217		11.7	3.44	0.84	2.60	6.20
24	0.0216		12.1	3.58	0.91	2.67	5.86
168	0 0214		11.7	3.85	0.99	2.86	5.78
335	0.0214		14.3	5.15	0.92	4.23	9.20

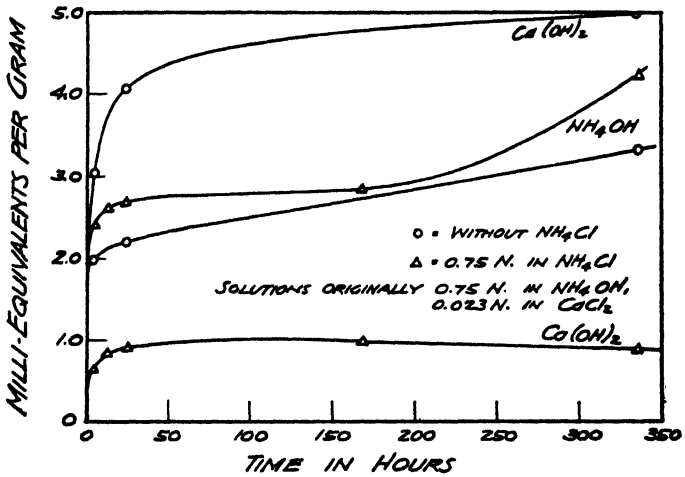

FIG. 6. TIME EFFECT. ADSORPTION FROM CALCIUM CHLORIDE–AMMONIUM HYDROXIDE–AMMONIUM CHLORIDE SOLUTIONS

TABLE 5

Adsorption of copper and ammonia (time effect)

0.2 g. of gel and 100 cc. of solution containing 0.025 *M* $Cu(NH_3)_4SO_4$ and excess of ammonia and ammonium chloride

TIME OF SHAKING	INITIAL NORMALITY		FINAL COPPER MOLARITY	GEL DISSOLVED	BASE ADSORBED MILLIEQUIVALENTS PER GRAM OF GEL			MOLAR RATIO NH_3 Cu ADSORBED
	NH_3	NH_4Cl			NH_3	$Cu(OH)_2$	Total	
hours	*N*	*N*	*M*	*per cent*				
4	0 10	0	0 0229	4 7	2 94	2 28	5 22	2 6
24	0 1	0	0 0220	4 5	3 76	3.14	6 90	2 4
168	0 1	0	0 0183	9 5	4 65	7 52	12 17	1 2
672	0 1	0	0 0171	8 6	4 71	8 70	13 41	1 1
4	0 1	0 50	0 0240	5 7	2 58	1 12	3 70	4 6
24	0 1	0 50	0 0236	10 1	3 20	1 72	4 92	3 7
168	0 1	0 50	0 0235	10 1	3 26	1 80	5 06	3 6
672	0 1	0 50	0 0234	9 0	3 01	1 81	4 82	3 3
4	0 75	0	0 0223	12 7	5 15	3 18	8 33	3 2
24	0 75	0	00218	26 0	6 55	4 22	10 77	3 1
168	0 75	0	0 0190	27 8	7 29	8 40	15 69	1 7
672	0 75	0	0 0184	29 0	8 41	9 34	17 75	1 8
4	0.75	0 50	0 0243	6 8	3 52	0 80	4 32	8 8
24	0 75	0 50	0 0239	14 6	4 38	1 30	5 68	6 7
168	0 75	0 50	0 0240	13 1	4 46	1 24	5 70	7 2
672	0 75	0 50	0 0240	13.6	5.74	1 18	6 92	9 7

Finally a set of experiments was carried out with mixtures of calcium and sodium hydroxide. Both bases were adsorbed, the adsorption of each of them being decreased by the presence of the other.

ADSORPTION OF COPPER FROM AMMONIACAL SOLUTION

The adsorption of the copper and total ammonia (as complex copper ion and free base) depends upon the time of shaking, and the concentration of copper, ammonia, and ammonium salt in the solution. From the results

TABLE 6

Adsorption of copper and ammonia from mixtures with various concentrations of ammonium chloride

0.5 g. of gel with 100 cc. of solution 0.025 *M* in $Cu(NH_3)_4SO_4$; 4 hours of shaking

INITIAL CONCENTRATIONS		FINAL Cu	GEL DISSOLVED	BASE ADSORBED MILLIEQUIVALENTS PER GRAM OF GEL			MOLAR RATIO NH_3/$Cu(OH)_2$ ADSORBED
NH_3	NH_4Cl			NH_3	$Cu(OH)_2$	Total	
N	*N*	*M*	*per cent*				
0.1	0	0.0197	1.7	2 75	2 18	4 93	2 5
0.1	0 1	0 0195	3 6	2 68	2.23	4 91	2 4
0.1	0 5	0 0221	4 3	2 30	1.25	3 55	3.7
0 1	1.0	0 0232	4 3	2 15	0 75	2 90	5 7
0.4	0	0 0177	5.9	3 70	3 28	6 98	2 3
0.4	0 5	0 0222	4.8	2.92	1.10	4 02	5 3
0.4	1.0	0 0235	4 2	2.57	0.54	3 11	9 5
0.75	0	0 0189	10 8	4 62	3.02	7 64	3 1
0 75*	0	0 0223	12 7	5 15	3.18	8 33	3 2
0.75*	0 5	0 0243	6.8	3.52	0 80	4 32	8 8
1.0	0	0 0192	14.1	4 90	3 00	7 90	3 3
1.0	0.5	0 0227	6.7	3 50	0 94	4 44	7 4
1.0	1.0	0 0238	6.2	3 11	0 46	3.57	13 5

* 0.2 g. of gel taken.

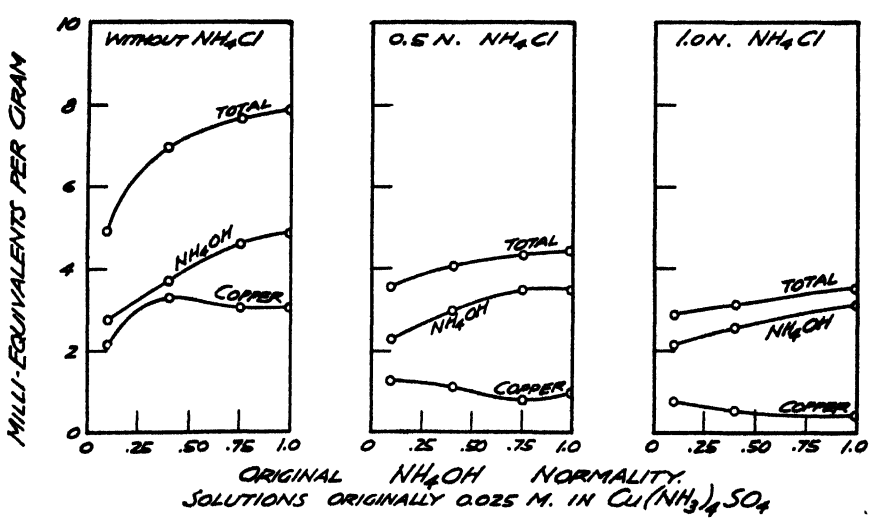

FIG. 7. FOUR-HOUR ADSORPTION FROM $Cu(NH_3)_4SO_4$–NH_4OH–NH_4Cl SOLUTIONS

in table 5 it is evident that no adsorption equilibrium is attained even after a long period of shaking. The molar ratio of ammonia to copper adsorbed decreases continuously with the time of shaking.

Ammonium chloride decreases the adsorption of copper and of the total base very strongly. This is clearly demonstrated by the figures in table 6 and the curves plotted in figure 7.

DISCUSSION OF THE RESULTS

1. Calcium hydroxide is much more strongly adsorbed by silica gel than the alkali hydroxides are. This could be expected, since the calcium silicate formed at the surface is very slightly soluble. From the investigations of Michaelis (8), Kühl and Wang Tao (7), and especially of Baylis (1), and of van der Burgh (9) there is no doubt that silica and lime react in a chemical way. The last author found that if enough calcium hydroxide is supplied to the lime a compound is formed with a molecular ratio of SiO_2 to CaO of 1:1, which is in equilibrium with a solution of 0.003 to 0.004 N calcium hydroxide. This compound can take up more lime (final molecular ratio, 1.4 CaO: 1 SiO_2). In our experiments there was always a large excess of silica, and the final concentration of the calcium hydroxide was often found to be smaller than 0.001 N. Therefore the concentration of calcium hydroxide in equilibrium with the solid phases, silica and calcium silicate, must be much smaller than that given by van der Burgh. In our experiments with calcium hydroxide alone and with mixtures containing ammonia, equilibrium was not attained even after ten days of shaking. This can be explained by the formation of insoluble calcium silicate in the pores of the gel resulting in a much slower rate of diffusion of the electrolyte in the interior of the gel.

2. Addition of ammonia promotes the adsorption of calcium hydroxide. At a concentration of ammonia of about 0.3 N, the lime adsorption reaches a maximum. At such high concentrations of ammonia the latter exerts a replacing effect upon the adsorbed calcium hydroxide, similar to that discussed in a previous paper (6).

Charriou (4) found the same effect of ammonia upon the coprecipitation of calcium with hydrous ferric oxide. The amount of calcium coprecipitated first increases, then reaches a maximum, and finally decreases with increasing ammonia concentration in the solution. He attributes the decrease to the formation of a complex compound between ammonia and calcium. However, from a special study to be reported later, it could be concluded that calcium hydroxide does not form complex compounds with ammonia even if the concentration of the latter is 2 N in the solution. It remains to be explained then why ammonia in smaller concentrations favors the adsorption of calcium hydroxide by silica gel. In the first place, it has to be considered that ammonia is much faster adsorbed than calcium hy-

droxide. It also exerts a dissolving effect and thus widens the pores of the gel. In order to prove this assumption, experiments were made in which the gel was shaken two hours with 0.1 *N* ammonia and then quickly washed with dilute acid and water. By such a process the adsorbent properties of the gel for calcium hydroxide had markedly increased, but not enough to account for the large effect noticed in the experiments described in table 3. Therefore, we have to assume that the adsorbed ammonia favors the chemical reaction between silica and lime. A solution of silica in dilute ammonia yields a white flocculent precipitate of calcium silicate upon the addition of calcium hydroxide. Such a precipitate is not noticed outside of the gel in the experiments with mixtures of calcium hydroxide and dilute ammonia. However, this reaction takes place in the interior of the gel, the adsorbed ammonia forming ammonium silicate, which has a tendency to diffuse out. On its way it meets the calcium hydroxide and forms the insoluble silicate in the interior of the gel. In many cases the gel becomes opaque by the calcium silicate formed. Summarizing then, the ammonia by its dissolving effect upon the gel widens the pores, and the ammonium silicate formed reacts in a chemical way with the calcium hydroxide in the interior of the gel.

3. Addition of ammonium salts decreases the pH and increases the solubility of the calcium silicate very markedly. Consequently, the adsorption of calcium hydroxide is strongly decreased by addition of ammonium chloride to a mixture of calcium chloride and ammonia. In a previous paper (6) a similar effect has been described of the influence of ammonium salts upon the adsorption of potassium hydroxide from a mixture of potassium chloride and ammonia.

4. The molecular ratio of ammonia to copper adsorbed is much greater than that formed under comparable conditions with ammonia and calcium. This and the dark blue color of the gel indicate clearly that the copper is first adsorbed as ammino complex. It is hard to say which complex of copper is adsorbed, since the ratio of NH_3 to Cu decreases with the time of shaking, whereas certainly part of the ammonia is adsorbed as such (compare with the adsorption of ammonia in the mixtures containing calcium). Berthon (2) claims that the copper is adsorbed as diammino complex by silica gel. As he made experiments after twenty-four hours of shaking only, it was quite accidental that he found a molecular ratio of ammonia to copper adsorbed of 2 to 1. Since part of the ammonia is certainly adsorbed as such, the ammonia content of his complex must have been less than two molecules per one copper. Experiments have been made in 0.1 *N* ammonia as reported in table 5, but in which the analyses were made after 15 minutes, 1 hour, and 2 hours of shaking. The molar ratios of ammonia to copper adsorbed were 3.6, 3.0, and 2.7. After one month of shaking the ratio decreased to 1.1. With higher concentrations of ammonia higher

ratios are found; here, however, the amount of uncombined ammonia adsorbed becomes much greater. From the figures in table 5 and by comparison with those in table 3 one may infer that at small ammonia concentration the copper is originally adsorbed as tri- or di-ammino complex. On further shaking this complex loses ammonia and finally approaches the composition of the monoammino complex. J. Bjerrum (3) from an extensive study concluded that various complex copper ammino ions exist, of the general formula

$$Cu(NH_3)_x(H_2O)_{4-x}^{++}$$

in which x may vary from 0 to 4. Upon prolonged electrodialysis practically all the ammonia could be removed from the gel, whereas all the copper remained behind.[2] The color of the gel during this process changed from blue to green. Originally all the copper in the solution was present as ammino complex. Therefore, first of all it had to be adsorbed as $Cu(NH_3)_x(H_2O)_{4-x}(OH)_2$ or more likely as $Cu(NH_3)_x(H_2O)_{4-x}SiO_3$, in which x had a value of approximately 2. This silicate is not in equilibrium with the solution, and on standing is transformed into $Cu(NH_3)(H_2O)_3SiO_3$. A different equilibrium therefore exists at the interface than in the solution. On electrodialysis the complex is forced to give off its last molecule of ammonia and the least soluble compound, aquo copper silicate, remains behind. The fact that the copper originally is adsorbed as ammino complex is also quite evident from the influence of ammonium chloride. The latter decreases not only the adsorption of the copper but also that of the ammonia very markedly (table 6), whereas in the case of calcium, which does not form a complex, the adsorption of ammonia is slightly increased (table 4).

5. The adsorption of calcium from ammoniacal solution is strictly comparable with that of copper, with the understanding that the former is primarily adsorbed as aquo ion and the latter as ammino ion which on standing returns ammonia to the solution.

SUMMARY

1. It has been explained why ammonia up to concentrations of 0.3 *N* promotes the adsorption of calcium hydroxide by silica gel.

2. The adsorption of calcium and copper is greatly decreased by the addition of much ammonium salt.

3. Copper from dilute ammoniacal solution is adsorbed as a complex ammino ion. At the surface it forms a silicate $Cu(NH_3)_2(H_2O)_2SiO_3$, which on standing is transformed into $Cu(NH_3)(H_2O)_3SiO_3$. Upon electrodialysis in water it loses its last molecule of ammonia.

[2] Experiments performed by Dr. W. G. Mitchell.

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ON THE ORIGIN OF THE ACTINIUM SERIES OF RADIOACTIVE ELEMENTS. II[1]

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We have recently discussed the origin of the actinum series in the light of F. W. Aston's mass spectrum analysis of uranium leads and our own measurements of the protoactinium: uranium ratio (12).

In the meantime, F. W. Aston has communicated new results at the Chicago meeting of the American Association for the Advancement of Science and has just published them (4). His results give fresh support to the actino-uranium theory and its discussion is warranted, especially since at the same meeting other views on the actinium series and their bearing on geological time measurements were expressed and our conclusions were far from being accepted.

I. THE ACTINO-URANIUM THEORY AND DISCUSSION OF LATEST RESULTS OF F. W. ASTON

The actino-uranium theory can be summarized as follows: The actinium series is independent of the uranium-radium series and is derived from actino-uranium (Ac-U), an isotope of uranium, which has a period equal to 4.0×10^8 years and which occurs in all the uranium minerals in a constant ratio to uranium I (U-I), independent of their age. The ratio of disintegrating atoms of actino-uranium to uranium I at our present geological epoch equals 4.0:100.

Aston's recent results on uranium leads, the chemical analysis of the minerals from which they were extracted, and other data pertaining to these minerals are given in table 1, which is also a continuation of table 1 from a preceding paper (Paper I, see reference 12).

The results with the Morogoro lead (column 4) are in complete agreement with the predictions of the actino-uranium theory, and the percentage of actinium D atoms found in this lead (7.4) is exactly the one to be expected from its age. (See figure 1, Paper I.)

The analysis of this lead is especially valuable because it is, like the Katanga lead, free from ordinary lead (as seen from the absence of the Pb^{208}

[1] Reported in part at the Chicago meeting of the American Association for the Advancement of Science, June, 1933.

TABLE 1

	4	6	7	8
1. Mineral	Pitchblende	Thorite	Broeggerite	Uraninite
2. Geographical origin	Morogoro, East Africa	Langesundfjord, Norway	Karlshus, Raade, Norway	Great Bear Lake, LaBine Point, Canada
3. Chemical analysis:				
Uranium, per cent	70.45¶	0 45†	61.16§	52.14**
Thorium, per cent	0.2 ¶	30 10†	4 38§	0.0
Lead, per cent	8.30¶	0 35†	8.02§	10 50**
4. Isotopic constitution of lead:				
Pb^{206}	93.1	4 6	86 8	89.8
Pb^{207}	6.9	1 3	7.3±0 2	7.9
Pb^{208}	0	94 1	3 7	2.3
			(a) (b)	
5. Percentage of RaG	93 1		85 5 86.3	88 5
AcD	6 9		6 4±0.2 6.9±0 2	7.0
ThD	0*		1 5 2.8	0 0
6. Chemical atomic weight of lead		207.90‡		close to 206 ††,**
7. Mean mass number	206 069	207 895		206 125
8. Ratio of lead to uranium	0 1178			0.201**
9. Ratio of radium G to uranium I	0 1093		0.1129	
10. Age in years	748×10^6		769×10^6	
11. Number of disintegrating protoactinium atoms for 100 decaying uranium I atoms	4 0 ±0 1¶			
12. Number of actinium D atoms for 100 atoms of radium G in uranium lead	7.4		7 5–8.0	

(a) Corrections made assuming $\lambda_{Th} = 4.0 \times 10^{-11} a^{-1}$, value of International Radium Standard Committee, 1931.
(b) Corrections made assuming $\lambda_{Th} = 6.0 \times 10^{-11} a^{-1}$, value of Geiger and Rutherford, corrected for $Z_{Ra} = 3.72 \cdot 10^{10}$ α/sec. & gr.
¶ A. V. Grosse and I. D. Kurbatov.
* The theoretical thorium D percentage calculated from the thorium content and using $\lambda_{Th} = 6 \times 10^{-11} a^{-1} = 0$ 09 per cent.
† Fajans K.: Sitzber. Heidelberg. Akad. Wiss. 1918, A, Abh. 3; Z. Electrochem. **24**, 164 (1918).
‡ Hönigschmid, O.: Z. Elektrochem. **25**, 91 (1919).
§ Analysis by C. N. Fenner and C. S. Piggot: Nature **123**, 793 (1929).
†‡ Report of the Committee on the measurement of geologic time of the National Research Council, p. 3 (1932).
** Private information from Dr. J. P. Marble for the same uraninite sample, from which the lead chloride used by us for the preparation of lead methyl was derived.

line), and therefore, the total amount of Pb^{207} found can be attributed, without any corrections, to actinium D.

The analysis of the Thorite lead (column 6), kindly supplied by K. Fajans, allowed F. W. Aston (5) to determine the "hydride effect," i.e., the contamination of a Pb^n with the $Pb^{n-1}H^1$ line. The effect was found to be 2.3 per cent of the line intensity and this correction has to be made for all his measurements.

We can also apply this correction to the Broeggerite lead, the first uranium lead to be analyzed by Aston (2), where the rather high values led A.

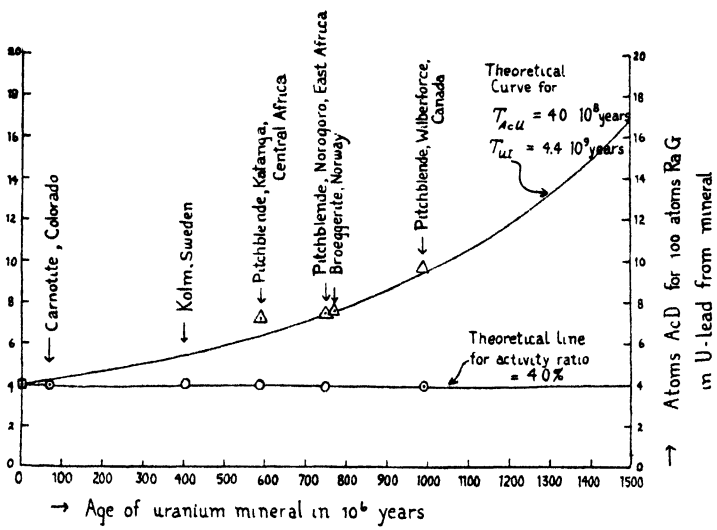

FIG. 1. THE ACTIVITY AND ACTINIUM D TO RADIUM G RATIOS AS A FUNCTION OF A MINERAL'S AGE

△ = ratio of actinium D to radium G in uranium lead determined directly by F. W. Aston with mass spectrograph.

⊙ = ratio of protoactinium to uranium I disintegrating atoms or activity ratio determined by A. V. Grosse and I. D. Kurbatov.

Holmes (13) to object to the actino-uranium theory. The corrected figures are given in column 7. From these the concentrations of radium G and actinium D are derived in the following way: We calculate the amount of thorium D from the thorium-content and approximate age of the mineral, and by subtracting it from the percentage of Pb^{208} we obtain the amounts due to isotopes of ordinary lead. Correcting Aston's values for these, we obtain the real percentages of radium G and actinium D. They are given in two columns corresponding to the two still disputable values of the disintegration constant of thorium, i.e., $\lambda_{Th} = 4.0 \times 10^{-11} a^{-1}$ or $6.0 \times 10^{-11}\ a^{-1}$.

The mean value for actinium D (7.7) again lies on the theoretical curve at the point corresponding to its age, which we derive in the most exact possible way from the radium G: uranium I ratio.

These results, combined with data of our previous paper are shown in figure 1. The agreement is far better than one could expect. The experimental results supplied by the mass spectrograph and the protoactinium: uranium activity ratio determinations can be explained satisfactorily only by the actino-uranium theory.

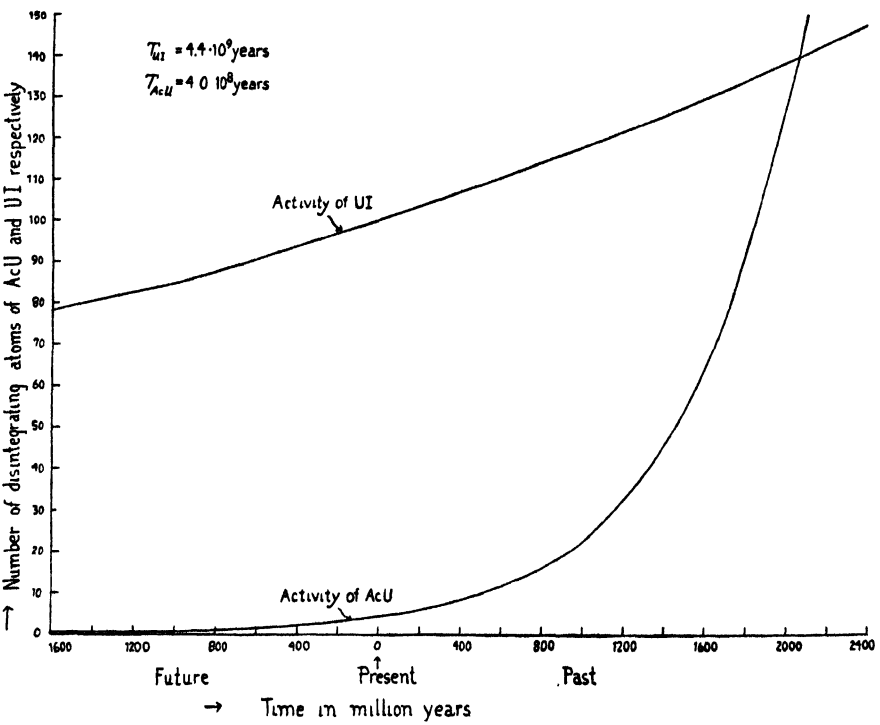

FIG. 2. ACTIVITY DUE TO ACTINO-URANIUM AND URANIUM I AS A FUNCTION OF TIME $T_{\mu I} = 4.4 \cdot 10^9$ years; value of International Radium Standard Committee, 1931

Figure 2 shows the activity due to actino-uranium and uranium I, respectively, as a function of time, and illustrates the actino-uranium theory in a simple way. We see how rapidly the actino-uranium activity increases as we go into the past; for instance, at the time of formation of Wilberforce uraninite (987 $\times$ 10^6 years ago) about twenty-two atoms of actino-uranium disintegrated for every one hundred and eighteen atoms of uranium I, whereas now it has dropped to four per hundred; this high initial quantity of actino-uranium in an old mineral of course now mani-

fests itself in the large amount of accumulated actinium D in the uranium lead.

Figure 2 is also instructive in another respect. The energy and heat evolution by members of the two series is directly proportional to the activity of the mother element, and we see how important a part the actinium series played in the heat balance and geological processes of the earth's crust in the early days of its history. The theories of J. Joly, H. Jeffreys, and A. Holmes will have to be reconsidered from this angle.

DISCUSSION OF OTHER THEORIES

We take this opportunity to discuss two theories which arose from other investigations.

1. A. Kovarik's theory (14) that the relative amounts of actino-uranium to uranium I and uranium II are initially the same, in all uranium-bearing minerals, is inconsistent with our protoactinium : uranium I ratio determinations; besides, it implies the unnatural idea that if an old uranium mineral, in which the actino-uranium has already decayed, goes into solution and a new uranium mineral forms from it, the actino-uranium will again be present in the initial ratio, appearing, so to speak, spontaneously.

2. E. R. Bishop (6, 8) and C. S. Piggot (16), interpreting the minima obtained from radioactive elements (1, 7, 10), using the magneto-optic method of F. Allison, have suggested schemes of four radioactive families, with eight isotopes of uranium, and Piggot (16) has discussed the significance of these findings in geological age determinations.

The radioactive schemes proposed contradict many well-established facts of radioactivity.

The *interpretation* of the minima is open to many objections and we think a clarification of the problem can best be accomplished by the use of definite radioactive elements as indicators.

The validity of the family schemes themselves can be easily checked with protoactinium. Contrary to the statement of E. Bishop (6) that no member of the actinium series has been isolated, pure protoactinium is available in centigram quantities (11) and since, according to E. Bishop (6) and C. S. Piggot(16) four isotopes of protoactinium exist, all of which gave birth to isotopes of the new elements "virginium" and "alabamine," their appearance in protoactinium preparations could be easily verified.

Even if the correctness of the family schemes suggested will be proven, which we doubt, the concentration and order of abundance of the individual isotopes still remain undecided. The statements concerning the last point are unclear and contradictory. The order of abundance of bismuth and thallium isotopes is absolutely against the mass spectrographic and chemical

atomic weight facts.[2] The following is another example: Piggot (16) assigns a magneto-optic minimum to radium B or Pb^{214}, presumably formed from traces of uranium, which he states are always present in lead salts; a simple calculation shows that from these uranium traces only a *fraction* of *an atom* of radium B can be formed in the whole apparatus, which we doubt even the magneto-optic method will be able to detect.

Under these circumstances, we consider the discussion of magneto-optic data premature. Even if they prove to be correct they would in no way affect the reliability of age determinations based on the experimental radium G:uranium I ratio.

THE GREAT BEAR LAKE PITCHBLENDE AND THE ACTINO-URANIUM THEORY'S CRITERION OF ALTERATION AND LEACHING

The only apparent exception to the actino-uranium theory is the Great Bear Lake pitchblende. It is reported (17) that this pitchblende has an age of about 1400×10^8 years and belongs to the oldest known; it is further reported (15) that it has a chemical atomic weight close to 206, suggesting an unusually small content of actinium D in uranium lead in contradiction to the demands of the actino-uranium theory.

On the other hand, this pitchblende shows definite signs of alterations; the mineral is tremendously brittle and traversed all over by veins, the larger ones seen with the unaided eye. Further, the lead:uranium ratio varies very much from sample to sample, i.e., from about 0.19 to 0.21, and in some cases reaches the limits 0.11 and 0.27 (17).

Aston's analysis (3) shows that the amount of actinium D is similar to the Morogoro and Broeggerite lead, indicating an error in the chemical atomic weight determination. Nevertheless the actual actinium D content is smaller than one would expect from the actino-uranium theory on the basis of its age, as given by the lead: uranium ratio. The theory demands, however, a relationship as expressed by formula 2 of Paper I *only* for *unaltered* minerals. Since the demands of the theory have been, as far as we see, sufficiently proven by experimental evidence, we can safely conclude that the lead: uranium ratio ($\simeq$0.20) does not give the real age of Great Bear mineral and some of the lead or uranium, or both, have been leached. We infer generally that if (in the age range up to 1×10^9 years) the age does not check with the actinium D : radium G ratio, leaching or alterations of some kind have taken place.

[2] Magneto-optic data indicate Bi^{211} and Bi^{210} to be the most abundant isotopes, whereas Bi^{209} is so far the only one found by Aston, in complete agreement with the chemical atomic weight 209.00; also the most abundant minimum of thallium is attributed to 207, whereas Aston (Proc. Roy. Soc. London **134A**, 577 (1932)) and also H. Schüler and J. E. Keyston (Naturwissenschaften **19**, 320 (1931)) found only 205 and 203, in agreement with the chemical atomic weight 204.39.

A safe estimate of the age of a leached mineral from this ratio alone is not possible, as the lead might be leached out to different extents at different times in the mineral's history; besides, there is always a possibility of infiltration of ordinary lead. This seems to be the case here as Pb^{208} is present (= 2.3 per cent), which can not be thorium D, since thorium is reported absent in the mineral (17). Summing up, the Great Bear Lake lead, because of alteration, cannot be used as evidence against the actino-uranium theory; instead, we have in the experimental actinium D:radium G ratio, a new check for alteration in uranium minerals.

FUTURE INVESTIGATIONS AND CONCLUSIONS

It is very important to continue the mass spectrographic investigations of uranium and thorium leads so successfully started by F. W. Aston. The mass analysis of the lead halides, instead of lead methyl,[3] would be desirable to avoid completely the correction due to hydride effect and to increase precision.

Data on the oldest obtainable uranium leads from minerals unaltered as far as possible are especially desirable, to test the applicability of the actinium D: radium G ratio formula beyond a billion years. (The Manitoba uraninite, for instance, discovered by H. V. Ellsworth (9), with a lead/uranium = 0.27 should prove worth while). They might also be interesting in another respect: In case the experimental curve should deviate in that range from our theoretical it might indicate the existence of a second actino-uranium isotope (still a possibility as we mentioned in paper I), not yet in equilibrium with our present isotope. The Rutherford-Soddy disintegration theory allows one to calculate in a simple way the ratio of actinium D to radium G for different possible cases; it would be, however, premature to discuss these points at the present time.

Besides supplying data for the development of the actino-uranium theory, the mass analysis allows one to determine, besides the isotopic constitution of the lead, the radium G:uranium I ratio, the exact age of the mineral and the atomic weight of the lead in a much shorter time and with greater reliability and accuracy than a chemical atomic weight determination.

SUMMARY

The latest mass spectrographic results of F. W. Aston with radiogenic leads are discussed and found to support completely the Piccard-Rutherford actino-uranium theory.

It is pointed out that the interpretation of magneto-optic minima by E.

[3] Perhaps the rapid advance in the Washburn method of concentrating H. Urey's H^2 will soon allow the preparation of $Pb(CH_3^2)_4$, where the hydride effect will of course not interfere in any way with the measurement of actinium D.

Bishop and C. Piggot and their schemes of radioactive families contradict well-established facts of radioactivity.

The anomaly of the Great Bear Lake pitchblende is traced back to alterations.

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ADHESION TENSION OF LIQUIDS AGAINST STRONGLY HYDROPHILIC SOLIDS

A Series of Liquids Against Barite

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The object of the present investigation was to improve and simplify the pressure of displacement method for measuring adhesion tension (1, 3, 4, 6, 11, 12), to adapt it for use with softer and less rigid materials than had previously been employed, and to obtain additional adhesion tension data with hydrophilic solid systems. It had been found that maximum pressure values obtained with receding liquid columns were more reproducible and more readily obtained than those determined with advancing liquid columns (8, 9). Accordingly pressures were measured which were just sufficient to cause the liquid column in the compressed powder membrane to recede.

APPARATUS

Since it had been found that the original hydraulic press method of packing cells caused crushing or cleaving of solid materials such as barite, new methods of packing the compressed powder membrane were studied. A tamping method of packing was finally adopted. Reproducible results were obtained by tamping even when the tamping plunger was operated by hand. Identical volumes were obtained by tamping the powder wet or dry. Hand tamping had the disadvantage that the force of impact of the packing plunger could not be measured in definite units, hence one investigator had difficulty in reproducing the results of another. A mechanical tamping machine was constructed which could be regulated so as to give definite and reproducible degrees of packing.

The cell to be packed was placed on a base, mounted on a stiff coil spring, which vibrated with each impact of the plunger. A packing guide directed the packing plunger as it fell into the cell. The plunger was raised by a small chain which passed through a pulley mounted above the cell. The pulley was adjustable and its position determined the distance of fall of the plunger. A rachet device attached to the chain released the packing plunger, which fell freely with each revolution of a hand-turned crank shaft. It was necessary to determine the weight of the packing plunger and the

distance of fall advisable for each solid. For the measurements with barite reported herein, a plunger weighing 360 g. was dropped 20 mm. fifty times with each added increment. About five 1-g. increments were used in the

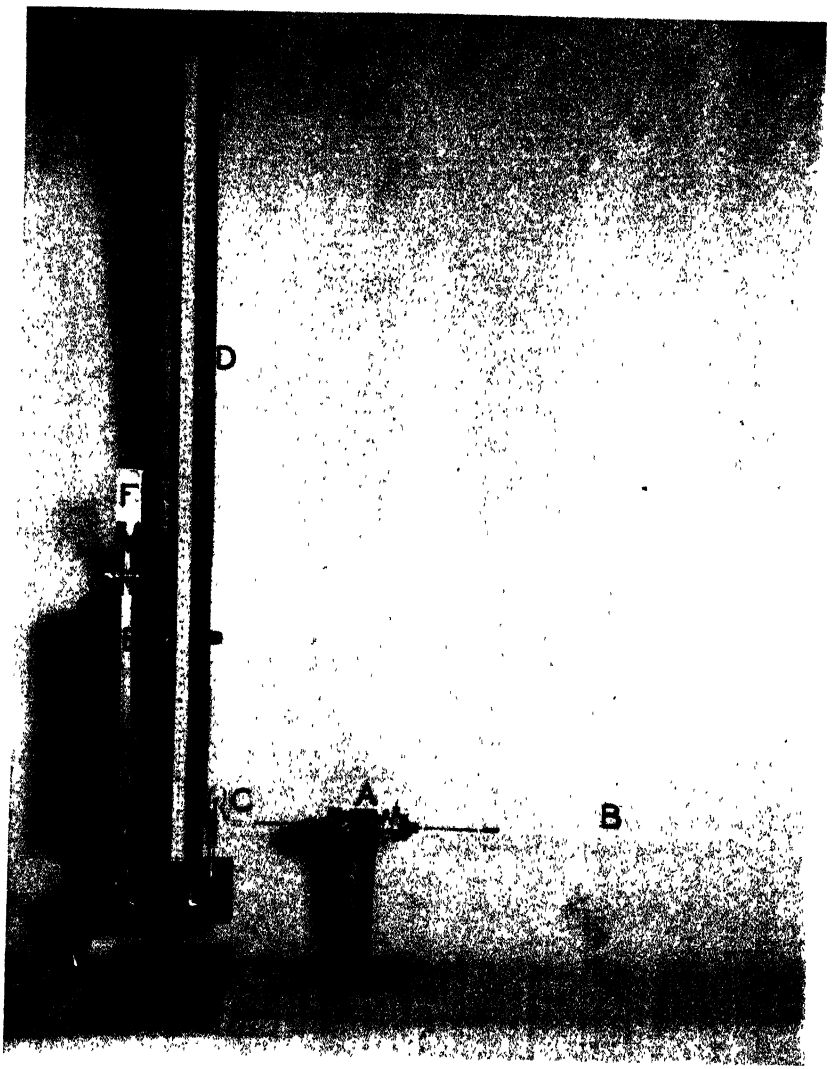

FIG. 1. CELL AND MANOMETER ASSEMBLY

A, displacement cell; B, indicator tube; C, bulb, intermediate section; D, manometer tube; E, auxiliary tube; F, mercury reservoir and drop control.

preparation of the membrane. A circular disc of linen cloth was placed in the cell before packing and a second disc was placed over the powder

during the tamping process and was left in place after the last tamping. The tamping method of packing eliminated almost entirely difficulties previously encountered which were traceable to improperly packed cells.

The displacement cell assembly used in this investigation is shown in figure 1. This apparatus is similar to that used by Bartell and Whitney (8). All measurements were made in a constant temperature thermostat held at 25°C. ± 0.1°C.

MATERIALS

The liquids used in this investigation were acetylene tetrabromide, benzene, carbon tetrachloride, heptane, butyl acetate and water. The liquids were all purified before use. In general, the purification was not rigorous, but was sufficient to give a reasonably pure product. The surface and interfacial tension values were determined for all the liquids.

The solid used was mineral barite, which contained less than one per cent of silicious material. The barite was heated in an electric oven for two hours at 400°C. and then ground in a ball mill. It was then washed with acetone (the very fine material was removed by decantation), dried for three hours at 110°C., and finally sifted through a series of screens to give definite particle size, 200 to 300 mesh.

METHOD OF MEASUREMENT

The graded powder was packed dry into the cell by tamping. The cell plunger was put in place and securely fastened. The liquid to be used was then drawn into the cell by suction until the powder was completely wetted, and the liquid column was caused to extend from the cell into the capillary indicator tube. For the pressure of displacement measurement of liquid–air systems the pressure was slowly built up by very fine drops of mercury which were caused to fall into the auxiliary arm E of the manometer D (see figure 1). As soon as the movement of liquid outward in the indicator tube was definite and constant, the auxiliary arm of the manometer was closed, leaving the manometer directly connected to the cell. The pressure in the manometer now continued to decrease as the liquid–air interface continued to move outward. Finally movement of the liquid column ceased and the pressure remained constant. This pressure was readily reproducible and was taken to represent the equilibrium pressure. The most consistent results were obtained when the interface was caused to come to rest near the middle of the membrane.

Measurements with liquid–liquid systems were carried out in a similar manner. The membrane was first wetted with the displacing liquid (for hydrophilic solids, water). In this case the indicator tube, B, was left full of liquid. The second liquid (organic liquid) was put into the glass bulb, C, which formed the intermediate section between the cell and manometer.

It was necessary to eliminate air completely from the liquid–liquid interface. This was accomplished by making a connection to the end of the indicator tube and applying enough pressure to cause the liquid in the cell to move through the small metal tube leading to the intermediate section. This section containing the organic liquid was tilted so as to bring the two liquids together and the interface, now free from air, was forced back into

TABLE 1

Adhesion tension measurements with barite

Air–organic liquid–barite

$r = 1.43 \times 10^{-3}$ cm.

LIQUID	P	$\cos \Theta_{12}$	Θ_{12}	S_2	A_{12}
	grams per cm².				
Acetylene tetrabromide	57 7	0 822	34°	49.07	40 5
α-bromonaphthalene	56 9	0 909	25°	44 00	39 9

P = Displacement pressure.
Θ_{12} = Contact angle solid–organic liquid–air.
Θ_{23} = Contact angle solid–organic liquid–water.
S_2 = Surface tension organic liquid.
S_{23} = Interfacial tension organic liquid against water.
A_{12} = Adhesion tension organic liquid against solid.
A_{13} = Adhesion tension water against solid.

TABLE 2

*Adhesion tension measurements with barite**

Water–organic liquid–barite

LIQUID	P	$\cos \Theta_{23}$	Θ_{23}	S_{23}	A_{12}	A_{13}
	grams per cm².					
Acetylene tetrabromide	50.7	0.928	22°	38.32		76.1
α-Bromonaphthalene	52.3	0.883	27°	41 57		76 6
Benzene	45.7	0 935	21°	34 31	44 3	
Heptane	61.8	0.877	28°	49.40	33.1	
Butyl acetate	16.8	0 896	26°	13.17	64.6	

* See footnote to table 1.

the membrane. Final connections to the manometer were made by means of ground glass joints and the procedure from this point was exactly the same as described for liquid–air systems.

DISCUSSION OF RESULTS

A summary of the adhesion tension values obtained for the different liquids against barite is given in tables 1 and 2. Each of the values is

the average of several separate determinations. The equations used and methods of calculating results have been presented in previous articles from this laboratory. The three liquids, benzene, carbon tetrachloride, and water were used to determine the pore radius (r). The radii as determined with these liquids showed excellent agreement. The adhesion tension values obtained for the series of liquids against barite were of the same order of magnitude as those which had been obtained for these liquids against silica (8) and against aluminum oxide (7). Table 3 gives the adhesion tension values obtained with five different liquids against these three different solids. In checking the data obtained in two hundred thirty-three different measurements made with these three different solids by the receding contact angle method, it was found that the largest average deviation in any one system was less than 1.5 per cent.

TABLE 3

Comparison of adhesion tension values for hydrophilic solids

SOLIDS	α-BROMONAPHTHALENE	ACETYLENE TETRABROMIDE	BENZENE	BUTYL ACETATE	WATER
Barite	39 9	40 5	44 3	64 6	76 4
Aluminum oxide (7)	40 1	43 0	45 0	64 5	76 7
Silica (8)	39 6	42 8	44 1	64 5	76 7
Silica (2) (Single capillary method)	41 1	43 3	45 4	66 6	75 9
Calcium fluoride (1)	43.0	—	50 1	65 2	76 5

The fact that these hydrophilic solids tend toward similar adhesion tension values indicates that they possess free surface energy values of the same order of magnitude.[1] It has been noted also that these solids exhibit similar behavior in settling experiments. With a series of liquids the degree of packing of the powders of these different solids on settling is always in the same order and usually of the same magnitude. It would be unreasonable to assume that all the solids per se possess the same free surface energy values. It would be more reasonable to assume that their surfaces when exposed to atmospheric conditions become altered. Probably water vapor

[1] Bartell and Osterhof (5) have pointed out that the adhesion tension values which they obtained for different liquids against Tripoli, based on a water-Tripoli value of 81.5 dynes, are about 6 dynes higher than the values obtained with the same liquids against other silicas by other investigators (2, 8). Their value of 81.5 dynes was established with the use of only one contact angle liquid, α-bromonaphthalene. We are inclined to believe that this one measurement is in error, inasmuch as the values they obtained with other liquids (assuming the reference value above mentioned to be in error) are similar to those obtained by other investigators. If it be true that this value is in error, it follows that the adhesion tension values of all the hydrophilic solids measured thus far give values of approximately the same magnitude.

is adsorbed. We are led to agree with other investigators (10, 13, 15, 16) that a primary water film is tenaciously adsorbed on the surface of hydrophilic solids and that the water molecules are definitely oriented.

Although considerable care has been exercised in all the displacement pressure researches in this laboratory to produce a reasonably clean surface on the solids used, it is doubtful if the procedure followed has prevented the formation of a water film (which may or may not be complete, i.e., it may be polymolecular or even monomolecular in thickness) on the capillary surfaces of the powdered membrane at some time before the final measurement was made. With the barite and aluminum oxide investigations conditions were certainly favorable for the formation of a complete water film, for the equilibrium pressure measurements were made by forcing the organic liquid into membranes which were already wetted by water. Under these conditions, however, it could be shown experimentally that this film was such that it possessed properties different from those of a liquid in mass. For example, when the organic liquid was forced into the water-wet barite membrane rapidly by building up an opposing pressure considerably above the equilibrium pressure and then the system allowed to come to an apparent equilibrium, in a short time a pressure was obtained which was the same as the pressure value demanded by a zero interfacial angle, that is a value of $A_{13} - A_{12}$ equal to the interfacial tension value of the organic liquid–water system was obtained. This indicated the presence of a complete water film, having the properties of a plane surface of water. In other words, this procedure gave a method, as had been previously pointed out (8), for measuring interfacial tension of organic liquid against water in water-wet capillaries. On the other hand, if the opposing pressure was built up slowly so that the organic liquid displaced the water slowly and the equilibrium pressure was only slightly exceeded, then a stable equilibrium condition was finally reached at a pressure lower than that demanded by the interfacial tension value. This indicated that a finite contact angle had formed and indicated further that no complete water film was present which possessed the property of a plane surface of water. The values given in tables 1 and 2 were obtained by the latter method.

It has previously been shown (2, 8) that the same values for adhesion tension of a given organic liquid against a solid are obtained by measurement of the solid–organic liquid–air contact angle as are obtained by measurement of the solid–organic liquid–water contact angle. The question may be raised as to the reliability of the adhesion tension data obtained with the pressure of displacement method, particularly with solids whose surfaces are not distinctly free from water films. Will data obtained enable one to detect differences in surface conditions of a strongly hydrophilic solid? The answer is that the data obtained are indicative of the nature of the surfaces as they actually exist, and that such data do enable one to predict the behavior to be expected with solids possessing such surfaces.

SUMMARY

A modification of the original pressure of displacement method for determining adhesion tension, termed a receding contact angle method, is described in some detail. This method is far more rapid, is easier to operate, and can be used with less danger of experimental error than the original method. An improved method is described for the preparation of membranes from finely divided powders. This method involves packing of powder by tamping. A tamping apparatus is described which gives a uniformly packed powder. The adhesion tension value of each of a series of liquids against barite is given. Comparison of the adhesion tension values of each of a series of liquids against each of several different hydrophilic solids shows that corresponding values are of very nearly the same magnitude. From this fact the conclusion is drawn that the surfaces of strongly hydrophilic solids are covered with an adsorbed film of water which gives to these solid surfaces such properties that their measured free surface energy values are of the same order of magnitude.

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ALTERATION OF THE SURFACE PROPERTIES OF STIBNITE AS REVEALED BY ADHESION TENSION STUDIES

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For adhesion tension studies, solids may be divided into two classes, hydrophilic solids which are wet more readily by water than by organic liquids, and hydrophobic solids which are wet more readily by organic liquids than by water.

Silica and oxides in general are hydrophilic. Carbon and various sulfides are hydrophobic. Quantitative experiments on Prussian blue indicate that it has non-selective wetting properties and is wet as readily by organic liquids as by water. Different hydrophilic solids show different degrees of preferential wetting by water, and different hydrophobic solids show different degrees of preferential wetting by organic liquids. In the present investigation a series of solids was sought whose wetting characteristics would cover the range from the extremely hydrophobic type to the extremely hydrophilic type. A major aim of this investigation was the correlation of the changes in free surface energy which occur when such a series of solids is wet by liquids.

Sulfides such as stibnite are slightly unstable at ordinary temperatures, and at slightly elevated temperatures they are readily oxidized. Preliminary tests showed that ordinary stibnite, Sb_2S_3, was hydrophobic, though not so strongly hydrophobic as carbon. Samples of stibnite were therefore subjected to successive limited oxidations to determine whether the material so treated could be caused to change its properties, step by step, from a hydrophobic solid to a hydrophilic solid.

PREPARATION OF MATERIALS

A quantity of relatively pure stibnite was ground and carefully graded. Samples of this stibnite will be referred to as stibnite A. Other samples of stibnite were prepared by heating stibnite A to 170°C. for different lengths of time. The series of stibnites was as follows:

Stibnite A = Unheated, finely ground stibnite graded to 250 to 300 mesh and air floated. Mixed thoroughly in a rotating cylinder for 2 hours.
Stibnite B = Stibnite A heated 1 hour
Stibnite C = Stibnite A heated 2 hours

Stibnite D = Stibnite A heated 3 hours
Stibnite E = Stibnite A heated 4 hours
Stibnite F = Stibnite A heated 5 hours
Stibnite G = Stibnite A heated 6 hours
Stibnite H = Stibnite A heated 8 hours
Stibnite I = Stibnite A heated 8 hours (400–420°C.) in a nitrogen atmosphere containing 0.7 per cent oxygen. This sample was graded to 250 to 300 mesh, but was not air floated.

Preliminary tests showed that stibnite I was hydrophilic and that each of the stibnites in the series with progressive degrees of oxidation was progressively less hydrophobic than stibnite A. It was observed also that if stibnite I were treated with hydrogen sulfide gas for a few minutes at a

TABLE 1

Adhesion tension data for water against different stibnites

Water–air–stibnite system

S_3 = 72.08 dynes per centimeter

STIBNITE	$r \times 10^{-4}$ CM.	P	$\cos \theta_{13}$	θ_{13}	A_{13}
		grams per cm²			*dynes per cm*
A	8 52	135	0 785	38°	56 5
B	8 52	137	0 794	37°	57.2
C	8.52	139	0 806	36°	58 1
D	8 52	144	0 836	33°	60 3
E	8.52	154	0 890	27°	64 2
F	8 52	159	0 922	23°	66 5
G	8 52	169	0 979	12°	70 5
H	8 52			0°	76 0*
I	11 1			0°	77 1*

* Values obtained from interfacial contact angle determinations.

slightly elevated temperature, it could be converted back into the hydrophobic type.

In addition to the stibnite powders, aluminum oxide was also used. It was graded to 300 to 350 mesh by sieving. The powder was treated twice with boiling hydrochloric acid (1:1) and allowed to stand in contact with the acid for several hours. It was washed six times with hot distilled water and was then washed twenty times with boiling distilled water while being filtered. It was dried at 110°C., then heated at 400° to 480°C. for 2 hours. The powder was thoroughly mixed, then heated at 510° to 530°C. for 8 hours and again mixed.

LIQUIDS

The water used was twice distilled and the accepted surface tension of 72.08 at 25°C. was used in all calculations for water.

The organic liquids used were very carefully purified and their surface

tensions and interfacial tensions against water were determined and used in all calculations.

METHOD AND APPARATUS

The displacement pressure cells and method used in this investigation for the determination of adhesion tension were the same as developed by

TABLE 2

Adhesion tension data for contact angle liquids against stibnites H and I

STIBNITE	LIQUID	$r \times 10^{4}$ CM	P	θ_{12}	$\cos \theta_{12}$	S_2	A_{12}
			grams per cm².			*dynes per cm.*	*dynes per cm*
H	α-Bromonaphthalene	8 52	104	8°	0 988	44 00	43 5
I	α-Bromonaphthalene	11 1	73 5	25°	0 910	44 00	40 0
I	Acetylene tetrabromide	11 1	79 8	28°	0 885	49 07	43 4

TABLE 3

Comparison of adhesion tension data of several liquids as determined against stibnite A and stibnite I

LIQUID	STIBNITE A (r = 8 52 × 10^{-4} CM)					STIBNITE I (r = 1 11 × 10^{-3} CM)		
	Surface tension	Interfacial tension	P	Cos θ_{23}	Adhesion tension	P	Cos θ_{23}	Adhesion tension
	dynes per cm	*dynes per cm*	*grams per cm²*		*dynes per cm*	*grams per cm².*		*dynes per cm*
1. Water	72 08	—	135	—	56 5	—	—	77 1*
2. Isoamyl alcohol	22 90	5 00	8 12	−0 679	59 9	5 70	0 621	74 0
3. *n*-Butyl acetate	24 06	13 17	23 0	−0 729	66 1	22.3	0 923	64 9
4. Benzene	28 22	34 31	52 3	−0 638	78 4	58 2	0 924	45 4
5. Acetylene tetrabromide	49 07	38 32	58 9	−0 642	81 1	79 8	—	43 4
6. α-Bromonaphthalene	44 00	41 57	68 2	−0 686	85 0	73 5	—	40 0
7. *n*-Heptane	19 80	49 40	69 9	−0 592	85 7	81.4	0 897	32 8

* Value obtained from interfacial contact angle determination.

Bartell and Jennings (3). The temperature was maintained constant in an air thermostat at 25°C. ± 0.05°C.

ADHESION TENSION AND CONTACT ANGLE MEASUREMENTS

From pressure of displacement measurements it was found that with progressive oxidation of the stibnite surface, the contact angle between water and solid decreased progressively. This is shown from the data presented in table 1. The adhesion tension values for water against all the solids except stibnite H and stibnite I were determined directly from the

solid–liquid–air displacement pressure data (4) and the values obtained ranged between 56.5 and 70.5 dynes per centimeter. Adhesion tension values for α-bromonaphthalene and acetylene tetrabromide against stibnite H and stibnite I were also determined directly. Having this latter

TABLE 4

Adhesion tension data of zero contact angle liquids against different stibnites

Water–organic liquid–stibnite systems

STIBNITE	$r \times 10^{-4}$ CM.	A_{13}	BENZENE				n-BUTYL ACETATE				α-BROMONAPHTHALENE			
			P	Θ_{23}	$\cos \Theta_{23}$	A_{12}	P	Θ_{23}	$\cos \Theta_{23}$	A_{12}	P	Θ_{23}	$\cos \Theta_{23}$	A_{12}
		dynes per cm.	*gm. per cm².*			*dynes per cm.*	*gm per cm².*			*dynes per cm.*	*gm. per cm².*			*dynes per cm.*
A	8.52	56.5	52.3	130°	−0 638	78 4	23 0	137°	−0.729	66.1	68.2	134°	−0 686	85 0
B	8 52	57 2	46.5	124°	−0 566	76 6	22 0	134°	−0.697	66 4	60.2	127°	−0 605	82 4
C	8.52	58.1	42.9	121°	−0 522	76 0	18 5	126°	−0 587	65 8	55 2	124°	−0 555	81 2
D	8.52	60.3	29.4	111°	−0 358	72 6	13 0	114°	−0 414	65 8	38 8	113°	−0 389	76 4
E	8.52	64 2		>90°				>90°				>90°		
F	8.52	66.5		<90°				<90°				<90°		
G	8 52	70.5	37 0	63°	−0.452	55 0	13 1	65°	−0 417	65.0	38 4	68°	−0 386	54 5
H	8 52	76.0	69.4	32°	−0 845	47.0	26 7	31°	−0 854	64 8	77 6	39°	−0 780	43 5
I	11.1	77.1	58 2	22°	−0.924	45.4	22 3	23°	−0.923	64 9	68 0	27°	−0 891	40 0

Interfacial angle <90°—water displaces organic liquid.
Interfacial angle >90°—organic liquid displaces water.

TABLE 5

Adhesion tension data for several liquids against aluminum oxide

$r = 8\ 42 \times 10^{-4}$ cm.

LIQUID	P	$\cos \Theta_{23}$	ADHESION TENSION
	grams per cm².		*dynes per cm.*
1. Water	—	—	76.7*
2. Isoamyl alcohol	6.77	0.556	73 9
3. n-Butyl acetate	29.4	0.924	64 5
4. Benzene	76 7	0.924	45 0
5. Acetylene tetrabromide	104	0 878	43 0
6. α-Bromonaphthalene	97	0 884	40 1
7. n-Heptane	105	0.877	33.4

* Value obtained from interfacial contact angle determination.

data, the adhesion tension value of water against each of the two solids was obtained indirectly from liquid–liquid–solid displacement pressure data by using in turn each of these organic liquids and water against each of the stibnites. Stibnite H gave an adhesion tension value with water of 76.0 dynes per centimeter, and stibnite I gave a value of 77.1 dynes per centimeter (table 1).

A comparison of adhesion tension data of several liquids against stibnite A and stibnite I may be made from the data given in table 3. Adhesion tension data for a series of liquids against the different stibnites are given in table 4. Data for a series of liquids against aluminum oxide are given in table 5.

CORRELATION OF ENERGY CHANGES OCCURRING ON THE WETTING OF SOLIDS

Bartell and Osterhof (1) had observed that when the adhesion tension values of carbon and silica were compared, the order of increasing adhesion

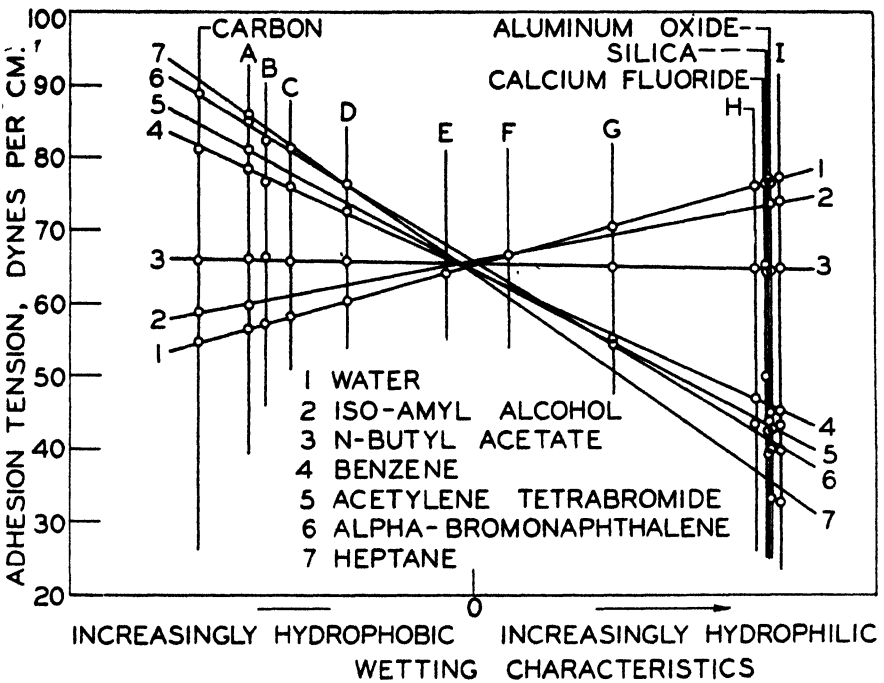

FIG. 1

tension values for the one solid against a series of liquids was just opposite to the order of increasing adhesion tension values of the other solid against this same series of liquids. They suggested (5) that the results might be correlated diagrammatically so as to show linear relationships for the adhesion tension values of a series of liquids against a series of solids when these values are plotted against the wetting characteristics of the solids. This proposed relationship had but little significance at the time, inasmuch as no adhesion tension data were available for systems whose wetting characteristics were intermediate between those of carbon and silica, with the exception of qualitative data on Prussian blue which showed that it was

wetted to practically the same degree by all the liquids used. Its wetting characteristics would then place it near the middle of such a diagram.

In this proposed diagram the adhesion tension values of the different liquids (i.e., liquids No. 1, 2, 3, 4, and 5) were to be plotted as ordinates and wetting characteristics, in arbitrary units, as abscissae. Such a diagram was constructed and an attempt was made to place the values for the different stibnites on it.

The adhesion tension values for carbon and silica were placed in vertical positions at the ends of the wetting characteristics axis. A straight "tie line" was drawn to connect the adhesion tension values for water against these solids. The positions for the adhesion tension values of water against the different stibnites were located upon this tie line and a vertical line drawn through each point. It was a fact of great interest that the adhesion tension values for the different liquids against each of the different stibnites were found to correspond to the ordinates of points on the "tie lines" set up between carbon and silica where these "tie lines" were intersected by the vertical lines. These relationships are shown in figure 1.

It may be noted that heat treatment of the original stibnite A for 1-hour and 2-hour periods had but little effect on the adhesion tension values. As the time of heating was increased, the surface energy changes were found to be greater and the state of the solid surface to have progressed toward that of the hydrophilic solids.

The adhesion tension values for water and for isoamyl alcohol against the solid were observed to have increased in a linear manner with increase of surface oxidation. The adhesion tension values for heptane, benzene, α-bromonaphthalene, and acetylene tetrabromide were observed to have decreased in a linear manner with increased oxidation. The adhesion tension of *n*-butyl acetate was observed to have remained at practically the same value for all samples of stibnite regardless of degree of oxidation. This liquid appeared to wet all the solids to practically the same degree.

The adhesion tension data for other solids against the same series of liquids were collected and also plotted (figure 1). The similar wetting tendencies of the hydrophilic solids should be noted.

It will be seen that as the middle of the diagram is approached from either side, the difference in energy levels becomes less and less, hence the degree of selective wetting of the different solids by given liquids becomes correspondingly less and less. At the center of the diagram the "tie lines" have almost a common point of crossing. If this were actually a common point, it would represent a "point of non-selective wetting." The interfacial contact angle at this point would be exactly 90°. If a solid possessed surface properties represented by this position on the diagram, it would be wetted equally well by all liquids (at least by liquids of the type of those studied). At this "point of non-selective wetting" all interfacial energy

levels would be the same, and hence the adhesion tension values of all liquids against the solid would be the same. In a displacement pressure cell there would be no displacement of liquid by liquid (organic liquid–water) in either direction. That liquid which wetted the powder first would not tend to be displaced by the second liquid. Stibnites E and F fall near the middle of the diagram. The difference in energy levels of the different liquids against these solids was so low that accurate measurement of them was not possible. Accordingly adhesion tension values of the organic liquids against these solids were not determined. Our only criterion of their surface condition (i.e., the hydrophilic or hydrophobic nature) was obtained through the adhesion tension value of water, which was determined by measurement of the solid–water–air contact angle.

In passing outward in either direction from this region of non-selective wetting, the difference in energy levels becomes greater and greater. The ease with which one liquid will displace another from the solid becomes correspondingly greater.

QUALITATIVE TESTS FOR THE DETERMINATION OF RELATIVE DEGREE OF WETTING

When the quantitative work of the relative degree of wetting had been practically completed, it was decided to make some qualitative tests which might give further and optically convincing evidence that the surface properties of the original stibnite had been altered in a definite and regular manner. It was hoped that those tests might be indicative of the practical importance of the data obtained. Two series of qualitative tests were run. One series will be designated as the "drop on powder test" and the other as the "degree of packing upon settling test."

Drop on powder test

In the first series of tests a drop of water was placed on smoothed out samples of the different powdered stibnites. When placed on stibnite A the drop appeared to give a large contact angle against the powder and showed no tendency to disappear into the powder, but persisted until the water evaporated. When the stibnites with the progressively altered surface characteristics were tested, the drops of water which remained upon them were progressively smaller and the contact angles formed likewise were progressively smaller. When water was placed on stibnites H and I no drops formed, the angle of contact of water against the solid was zero, the water wetted the stibnite completely and disappeared entirely into the powder. The results obtained in this series of tests were what one might expect to obtain with a series of powders with surface properties ranging from strongly hydrophobic to strongly hydrophilic.

Degree of packing on settling test

In the second series of tests the powdered solid was suspended in liquid media and observations were made of the degree of packing of the powder on settling. This test was suggested by work previously done on "liquid absorption" (1, 2). Altogether six separate experiments were run.

The six experiments were as follows: (1) water, (2) *n*-butyl acetate, and (3) α-bromonaphthalene, with each of the nine different stibnites, and (4) stibnite A, (5) stibnite E, and (6) stibnite I with each of the seven different liquids.

In each of the experiments 10 g. of powder, together with 7 cc. of liquid, was put into each of a series of test tubes of uniform diameter, thoroughly

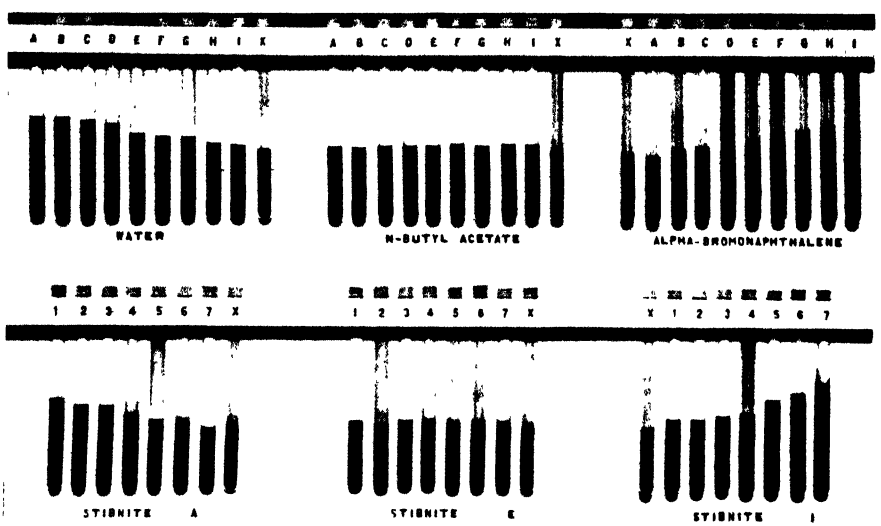

FIG 2

mixed, and allowed to settle. The stibnite samples were similar to, but not the same as, those that were used in the adhesion tension work. The tests were made upon finely ground, ungraded stibnite which had been subjected to the same treatment as the previously described samples of graded powders. The symbols used to indicate the different heat treatments are the same as those used for the graded powders. The liquids used were numbered as for the adhesion tension experiments, viz., 1 = water, 2 = isoamyl alcohol, 3 = *n*-butyl acetate, 4 = benzene, 5 = acetylene tetrabromide, 6 = α-bromonaphthalene, and 7 = *n*-heptane. The test tubes labeled X contain 10 g. of stibnite, but no liquid medium.

A photograph of the tubes, figure 2, clearly presents the results obtained. The photograph was taken about a week after the settling test was started.

After four months the heights of the settled powders were practically unchanged. A similar set of settling tests made with finely divided silica (Silex) gave similar effects upon settling and the heights of the different powders have remained unchanged for a period of over two years.

The results obtained in each of the six experiments mentioned may be briefly summarized in the statement that the degree of packing of the powder upon settling is greatest in that liquid against which it possesses the greatest adhesion tension and is progressively less in those liquids against which it has a progressively lesser adhesion tension.

The experiments showed conclusively that the surface properties of the stibnites were altered by the simple heat treatment. They showed that it is possible to alter greatly the preferential wetting properties of certain solids; that one can cause surfaces to function either as hydrophobic or hydrophilic surfaces. Moreover, it is possible to reduce surfaces to a condition in which they show no selective wetting tendency, that is, they are preferentially wetted neither by water nor by organic liquids.

In the present paper we shall make no attempt to discuss the character of the different surfaces studied, nor of the theories pertaining to the change in surface properties. It may be of interest to mention that the appearance of the surfaces was unaltered, the particle size of the powder was unaltered, and the pore radii formed with each sample of the different graded powders were the same. This work is being considerably extended in our laboratories and we expect to present more comprehensive generalizations in the near future.

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X-RAY STUDIES ON THE HYDROUS OXIDES. IV

TITANIUM DIOXIDE

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Tetravalent titanium, like tin, is said to form two distinct acids: ortho- or alpha titanic acid and meta- or beta titanic acid. Since the work of several investigators has shown that the stannic acids (13) are in reality hydrous stannic oxides differing essentially in the size of the primary particles, it seems not unlikely that the so-called titanic acids are also hydrous oxides whose properties are determined by the size and physical character of the particles.

The product commonly called orthotitanic acid, or alpha titanic acid, is a white gelatinous precipitate formed by the addition of ammonia or alkali hydroxide to a solution of a tetravalent titanium salt. The highly hydrous gel is readily soluble in dilute acids and is easily peptized by dilute alkalies and suitable salts to give stable sols. On the other hand, the product referred to as meta titanic acid, or beta titanic acid, is a granular, difficultly soluble, and but slightly peptizable substance obtained (a) by the interaction of nitric acid and titanium, (b) by the aging under water of the precipitated gel of the so-called orthotitanic acid slowly in the cold and more rapidly in the hot, (c) by precipitation in the hot, and (d) by hydrolysis of solutions of tetravalent titanium salts.

The composition of the preparations referred to above varies with the method of precipitation and with the subsequent treatment. The only evidence for the existence of definite hydrates corresponding to the formulas of the acids that earlier investigators (2, 5, 9, 10, 11, 12) have assumed, is the analysis of the products formed and dried under arbitrary conditions. Carnelly and Walker (1) obtained a smooth temperature–composition isobar for a precipitated gel and hence concluded that no definite hydrates were formed, unless it is assumed that a large number exist, each stable over a very narrow temperature range. Morley and Wood (8) prefer to assume that the change from the so-called alpha to beta form consists of a condensation to complex salt-like compounds, but there is no experimental justification for this point of view. More recently Gutbier and coworkers (3) obtained smooth composition–temperature isobars for several preparations, indicating the absence of definite hydrates of titania.

No systematic study of the constitution of the alleged titanic acids has been made by the x-ray diffraction method. Hedvall (4) states that "titanium hydroxide" precipitated at some unspecified temperature is crystalline, since it gives a good interference pattern both when moist or when dried at room temperature. On the other hand Gutbier and coworkers (3) report that the freshly precipitated products give no interference pattern, but the gels thrown down with ammonia at 20°C. to 100°C. and subsequently ignited give the pattern of the mineral rutile or a mixture of rutile and anatase, and the product obtained by oxidizing $Ti_2O_3 \cdot xH_2O$, followed by heating to 490°C., gives the x-ray pattern of anatase.

In the following section will be given the dehydration isobars of two typical gels of titanium dioxide and the results of the x-ray examination of precipitated oxides obtained under widely varying conditions.

EXPERIMENTAL

1. *Preparation of samples*

Precipitation with ammonia. A solution of 17 g. of titanium tetrachloride in 75 cc. of 6 *N* hydrochloric acid was treated with ammonia at room temperature and the resulting precipitate washed thoroughly by decantation by the aid of the centrifuge until only a trace of chloride remained. This sample, which will be designated as No. 1, was treated in different ways, as given in table 2. A second sample, designated as No. 6, was prepared by treating a boiling solution of the tetrachloride with a small excess of ammonia, boiling the mixture for 15 minutes, and finally washing and drying like sample No. 1.

Oxidation of $Ti_2O_3 \cdot xH_2O$. A solution of 8 g. of titanium trichloride in 100 cc. of water was treated with 15 cc. of 15 *N* ammonia, the mixture diluted to 400 cc. and allowed to oxidize in the air. The original black precipitate changed rapidly to a gray color which changed slowly to white on conducting a current of air into the suspension. This precipitate (No. 2) was thoroughly washed and air-dried at room temperature.

Hydrolysis. A dilute solution of titanium tetrachloride in hydrochloric acid was hydrolyzed by boiling for four hours, using a reflux condenser. The resulting granular precipitate was washed with hot water and air-dried at room temperature. Similar preparations were made by hydrolysis of the nitrate and sulfate.

2. *Isobaric dehydration*

Temperature–composition isobars for sample No. 1 precipitated at room temperature and sample No. 2 made by oxidation of $Ti_2O_3 \cdot xH_2O$ were obtained in the following way. The samples in glass-stoppered weighing bottles were placed in a thermostated electric oven through which dry air was circulated at the rate of 72 liters per hour. The air was dried by

passing it through a large calcium chloride tower, a sulfuric acid bottle, and finally through a tower filled with glass wool and phosphorus pentoxide.

TABLE 1

Thermal dehydration isobars of hydrous titanium dioxides

TEMPERATURE	COMPOSITION MOLES H_2O/TiO_2		TEMPERATURE	COMPOSITION MOLES H_2O/TiO_2	
	No 1 Pptd at room temperature	No 2 Oxidation of Ti_2O_3 xH_2O		No 1 Pptd at room temperature	No 2 Oxidation of Ti_2O_3 xH_2O
degrees C.			*degrees C*		
35 1	0 970	1 030	122 5	0 288	0 291
71 3	0 562	0 590	150	0 218	0 217
87 2	0 425	0 454	184	0 184	0 154
92 6	0.415	0 402	205	0 114	0 101
100 0	0.362	0 361	224	0 081	0 084
105 4	0 308	0 306	255	0 054	0 061
110 0	0 295	0 296	270	0 046	0 053

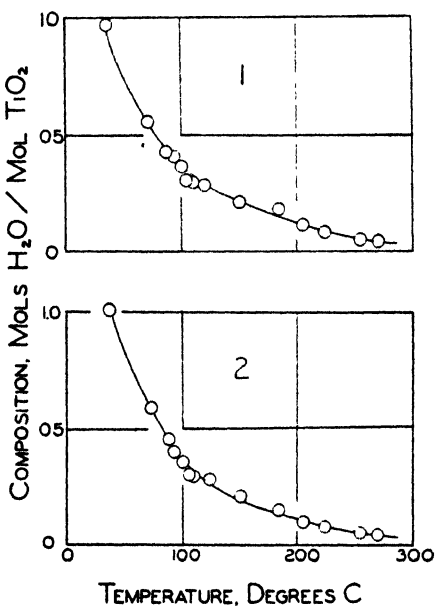

FIG. 1. DEHYDRATION ISOBARS OF HYDROUS TiO_2

1. Precipitated at room temperature. 2. Made by oxidation of $Ti_2O_3 \cdot xH_2O$ in air.

The rate was measured with a calibrated oil-filled flow meter left permanently in the line. The air was filtered through cotton just before passing into the oven. The air was preheated by passing through a 15-foot coil of

glass tubing inside the oven and was then conducted into a small enameled pan with a loose fitting cover, which held the samples. This arrangement is similar to that of L. H. Milligan (6). The temperatures were measured with standardized thermometers and a standardized thermocouple. The temperature was kept constant to within 1 to 2°C. To attain equilibrium conditions at a given temperature, each sample was heated at least four days and in some cases for as long as thirty days. In general, less time was required to attain equilibrium at higher than at lower temperatures. The results are given in table 1 and figure 1. In agreement with the results of Gutbier, the smooth isobars for both samples indicate the absence of hydrates of the oxide corresponding to the alleged acids.

TABLE 2

X-ray examination of hydrous titanium dioxides

SAMPLE NO	METHOD OF PREPARATION	RESULTS
1	Precipitated at room temperature	No visible lines or bands
3a	No. 1 aged at room temperature 14 weeks	No visible lines or bands
3	No. 1 aged at room temperature 30 weeks	Anatase pattern, very broad bands
5	No. 1 aged 6 hours at 100°C.	Anatase pattern, broad bands
4	No. 1 heated to 184°C.	Anatase pattern, broad bands
11	No. 1 heated to 1000°C.	Rutile pattern (and trace of anatase?)
6	Precipitated at 100°C.	Anatase pattern, broad bands
2	Oxidation of $Ti_2O_3 \cdot xH_2O$	No lines or bands visible
14	No. 2 heated to 184°C.	No lines or bands visible
12	No. 2 heated to 1000°C.	Rutile pattern (and trace of anatase?)
9	Hydrolysis of $TiCl_4$	Rutile pattern, broad bands
9a	Hydrolysis of $Ti(NO_3)_4$	Rutile pattern, broad bands
7	Hydrolysis of $Ti(SO_4)_2$	Anatase pattern, broad bands
10	Mineral rutile, TiO_2	Rutile pattern, sharp lines
8	Mineral anatase, TiO_2	Anatase pattern, sharp lines
13	Mineral brookite, TiO_2	Brookite pattern, sharp lines

3. X-ray analysis

The specimens listed in table 2 were examined as described in preceding papers of this series. The diffraction data are given in table 3 and are shown in chart form in figure 2 for purposes of comparison.

Densitometer curves of the films from samples 1, 4, 6, and 8 are given in figure 3. These curves were obtained with a simplified and inexpensive recording photodensitometer that has already been described (7). From these data it is apparent that the samples precipitated in the cold give little or no x-ray diffraction pattern, whereas both the aged oxide and the one thrown down at 100°C. give the anatase pattern. The precipitate freshly

formed in the cold consists either of amorphous TiO_2 with adsorbed water or, what is more likely, of anatase crystals so minute that little or no x-ray diffraction effect is observed.

As already noted, Hedvall obtained an x-ray diffraction pattern with a precipitated titania. Since both Gutbier and ourselves failed to get a pattern with the cold precipitated oxide, it is probable that Hedvall's

TABLE 3

X-ray diffraction data

SAMPLE NO 4 (Heated at 184°C.)		SAMPLE NO. 5 (Aged at 100°C.)		SAMPLE NO 6 (Pptd. at 100°C)		SAMPLE NO 8 (Anatase)		SAMPLE NO 9 (Hydrolysis of $TiCl_4$)		SAMPLE NO 10 (Rutile)		SAMPLE NO 11 (Heated at 1000°C)		SAMPLE NO. 12 (Heated at 1000°C)	
D	I	D	I	D	I	D	I	D	I	D	I	D	I	D	I
3 50	10	3.50	10	3 50	10	3 49	10	3 24	10	3 24	10	3 51	1	3 23	10
2.37	5	2 37	6	2 37	5	2 37	5	2 48	8	2 48	9	3 24	10	3 00	1
1 890	8	1 890	8	1 890	8	1 883	8	2 18	3	2 29	1	2 48	8	2 84	1
1 669	5	1 695	5	1 694	6	1.695	6	2 045	2	2 18	4	2 29	1	2 47	8
1 472	5	1 670	5	1 675	6	1 655	6	1 685	10	2 04	2	2 18	5	2 29	1
1 260	4	1 480	5	1 471	5	1 477	5	1 616	3	1 685	10	2 05	2	2 18	3
1 160	3	1 360	2	1 356	1	1 358	2	1 480	2	1 617	3	1 895	1	2 11	1
		1 340	2	1 260	4	1 334	2	1 360	8	1 479	2	1 685	10	2 04	1
		1 261	3	1 160	3	1 261	4	1 337		1 448	2	1 623	3	1 89	1
		1 162	1			1 161	3	1 090	1	1 351	8	1 481	1	1 788	1
		1 04	1			1 044	2	1 038	1	1 240	1	1 450	1	1 683	10
						1 015	2			1 167	1	1 359	8	1 617	4
						0 951	1			1 144	1	1 242	1	1 474	1
						0 913	1			1 092	1	1 169	1	1 444	1
						0 892	1			1 037	1	1 145	1	1 428	1
						0 876	1					1 092	1	1 359	4
						0 843	1					1.039	1	1 345	4
						0 824	1							1 240	1
						0 806	1							1.167	1
						0 795	1							1 145	1
						0 740	1							1 093	2
						0 702	1							1 038	2
						0 668	1								

precipitate was obtained in the hot and that the pattern showed the lines of anhydrous TiO_2 (anatase modification) as we observed.

The samples ignited at about 1000°C. consist for the most part of rutile. Inspection of table 3 shows that sample No. 11 gives in addition to the rutile pattern very weak lines at 3.51 A.U. and 1.895 A.U. It will be observed that the two most intense anatase lines are 3.49 A.U. and 1.883 A.U. It seems likely that a small amount of unchanged anatase is present in this ignited sample. Sample No. 12 also consists of rutile with the

addition of lines of weak intensity at 3.00 A.U., 2.11 A.U., 1.89 A.U., and 1.79 A.U. Since the sample was precipitated originally from $TiCl_3$ solu-

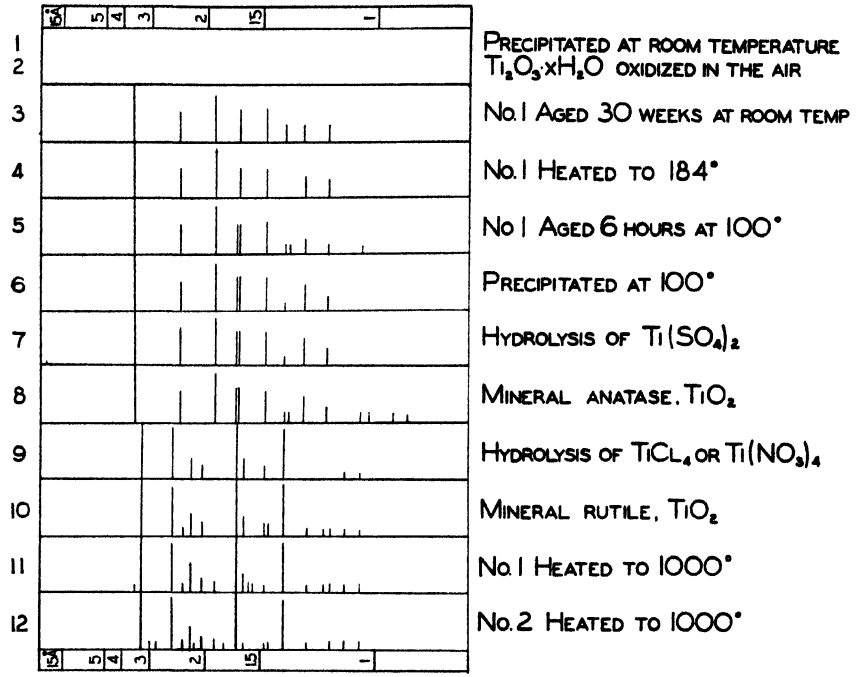

FIG. 2. CHART OF X-RAY DIFFRACTION PATTERNS

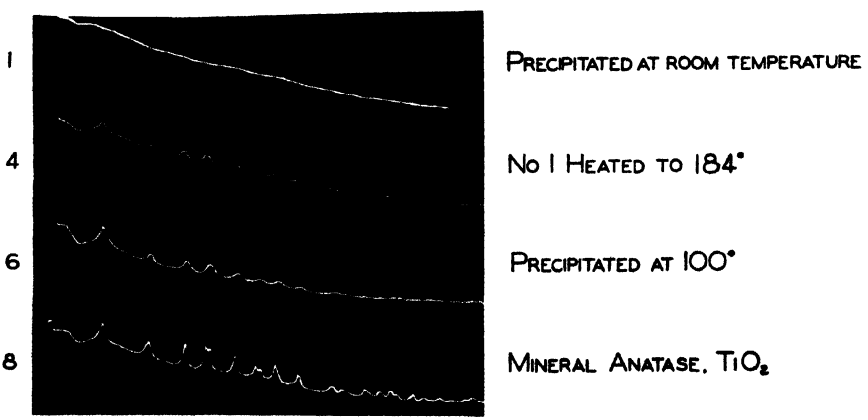

FIG. 3. DENSITOMETER CURVES OF X-RAY DIFFRACTION PATTERNS

tion and oxidized in the air, it may contain some impurities not present in the other samples.

SUMMARY

The following is a brief summary of the results of this investigation:

1. X-ray diffraction examination of hydrous titanium dioxide freshly precipitated at room temperature or freshly prepared by the oxidation in air of $Ti_2O_3 \cdot xH_2O$ gives no lines or bands. Thermal dehydration isobars for these two samples show the water to be given off in a continuous manner. The dehydration experiments of Gutbier and coworkers for their similar samples are confirmed. There is no indication of the existence of any definite hydrate.

2. Aging under water at room temperature for fourteen weeks of hydrous titanium dioxide precipitated at room temperature produces no change detectable by x-ray diffraction methods. Further aging of this sample for thirty weeks at room temperature or for 6 hours at 100°C. under water, gives minute anatase crystals; heating of the freshly formed material to 184°C. gives anatase.

3. Hydrous titanium dioxide precipitated at 100°C. shows the x-radiogram of anatase.

4. Hydrous titanium dioxide prepared by the hydrolysis at the boiling point of solutions of titanium tetrachloride and titanium nitrate, shows the x-radiogram of rutile, whereas hydrolysis of titanium sulfate under similar conditions gives anatase.

5. The product obtained by ignition at approximately 1000°C. of the hydrous oxide precipitated in the cold, shows the x-radiogram of rutile with indications of the presence of a little unchanged anatase.

6. X-ray analysis and thermal dehydration isobars indicate that no definite hydrates of titanium dioxide have been prepared.

7. Precipitated titanium dioxide is a hydrous oxide consisting, especially when precipitated or aged in the hot, essentially of anhydrous TiO_2 (anatase modification) and adsorbed water.

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HIGH CONCENTRATIONS OF RADIUM AND MESOTHORIUM I IN NATURE AND REGULARITY OF THEIR MIGRATION

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All beds of radioactive ores, as is well-known, are accumulations of uranium minerals. Accumulations of radium in large quantities have not been known without uranium and ionium. Usually it is considered that in nature there are neither concentrations of radium without parent elements nor separate radium minerals without uranium. Therefore, an individual geochemistry of radium without uranium and ionium seemed to be scarcely possible, owing to the short life of radium in the solid crust.

However, during the last few years several authors have published papers discussing discoveries of unexpected radium concentrations in natural waters (18), in which the radium was unaccompanied by corresponding equilibrium amounts of uranium.

The first papers, with results of analyses, were published in the Russian language and gave a great amount of material which is very interesting from many points of view. Namely, in the region of petroleum beds, some salt springs were discovered which contained radium in quantities up to 1.8×10^{-8} g. per liter of water.

Similarly, it was found by Cherepennikov that the spring which issues from the pit-hole "Kasennaya No. 1" in the petroleum district of Uchta in the northeastern part of European Russia contains 7.4×10^{-9} g. of radium per liter of water (4).

The precise radioactive and chemical analysis of the water of this pit-hole was carried out in the radiological laboratory of the University of Moscow, where the concentration of radium mentioned above was confirmed and a high concentration of mesothorium I was also found to be present.

Analyses of radium in the water from Grosny petroleum district were carried out in the Radium Institute of Leningrad and showed that the pit-holes No. 1/28, 3/28, and 1/31 contain 1.83×10^{-8} g. of radium per liter of water and that pit-hole No. 31/13 contains 3.5×10^{-9} g. of radium per liter of water (5).

The greatest amount of radium in the water of mineral wells and springs known previously was discovered by A. Becker (1) in the Radium-Sol-Terme of Heidelberg. It amounts to 1.79×10^{-9} g. of radium per liter of

water, that is to say, the concentration is one-tenth of that in the new found radium-containing salt waters which are associated with the petroleum beds.

In table 1 are given the highest concentrations of radium in the newly found mineral springs under discussion and for comparison, the content of radium in the Radium-Sol-Terme of Heidelberg. In table 2 are given concentrations of radium discovered in the water of some other springs, together with old analyses of rich radium springs.

TABLE 1

Springs with the highest concentrations of radium

NAME AND GEOGRAPHICAL SITUATION OF THE SPRING	DEPTH OF THE PIT-HOLE AND OTHER CHARACTERISTICS OF THE WATER	CONTENT OF RADIUM IN GRAMS PER LITER OF WATER	AUTHOR
Pit-holes No. 1/28, 3/28, 1/31. Petroleum district Grosny. North Caucasus, Russia	600–700 meters. Layers of Chokraksky. Layer 13. Water without petroleum, contains SO_4^{--} ions	$1\ 8 \times 10^{-8}$	B. A. Nikitin (1930)
Pit-hole No. 31/13. Petroleum district Grosny. North Caucasus, Russia	About 450 meters. Layers of Chokraksky. Layer 1. Water with petroleum emulsion contains SO_4^{--} ions	$3\ 5 \times 10^{-9}$	B. A. Nikitin (1930)
Pit-hole "Kasennaya No. 1." Petroleum district of Uchta. Northeastern European Russia	Water without petroleum contains Ba^{++} and Cl^-; does not contain SO_4^{--} ions	$7\ 4 \times 10^{-9}$	V. I. Baranov, I. D. Kurbatov, A. A. Cherepennikov (1928)
Radium pit-hole of Heidelberg in Germany	Depth of 998 meters. Salt-Terme	$1\ 79 \times 10^{-9}$	A. Becker (1918)

The second fact of importance is the great flow of water, and accordingly the large quantity of radium brought up to the surface of the earth. The quantity of radium carried up by a group of springs in a single district often amounts to more than one gram per year.

Two scientific problems of special interest arise from these discoveries: (1) the geochemistry of radium, apart from that of uranium, in the earth's crust; (2) the development of a technique for separating the radium from salt waters without the necessity of using a large quantity of reagents.

MIGRATION OF THE RADIOACTIVE ELEMENTS RADIUM, MESOTHORIUM I, THORIUM X, AND RADIOTHORIUM IN NATURE

In studying the geochemistry of radium, it must first be made clear whether radium and its isotopes are formed directly from their parents in

TABLE 2

Springs of high radium concentrations

NAME AND GEOGRAPHICAL SITUATION OF THE SPRING	DEPTH OF THE PIT-HOLE AND OTHER CHARACTERISTICS OF THE WATER	CONTENTS OF RADIUM ELEMENTS IN GRAMS PER LITER OF WATER	AUTHOR
Pit-hole No. 1/35. Petroleum district of Grosny. North Caucasus. Russia	More than 1000 meters. Layer 22. Water with petroleum odor contains SO_4^{--} ions	$3\ 0 \times 10^{-10}$	B. A. Nikitin (1930)
Pit-hole Stolb Berecley. Petroleum district Dagestan in Caucasus. Russia	—	$3\ 0 \times 10^{-10}$	A. A. Cherepennikov (1928)
Spring Slavyanovsky. Watering place of Gelesnovodsk. North Caucasus. Russia	About 50 meters. The water is running from the trachyts of the Gelesnaya (mountain). Contains SO_4^{--} and Cl^- ions	$2\ 21 \times 10^{-10}$	I. D. Kurbatov V. Baranov (1928)
Karlsbad, Czechoslovakia	Sprudel (9, 11)	1.0×10^{-10} 0.35 to 0.54×10^{-10}	W. Kolhorster (1912) H. Mache and F. Kraus (1928)
Saratoga, New York, America (12, 15, 16)	—	1.1×10^{-10} to 1.0×10^{-10}	H. Schlundt (1909), R. B. Moore and C. F. Whittemore (1914)
Bath, England (13)	—	1.4×10^{-10}	W. Ramsay (1912)

the mineral water of the spring, or whether they are extracted from the neighboring rocks.

The parent substance of radium is ionium, that of mesothorium I is thorium, and that of thorium X is radiothorium. If radium and its isotopes are formed directly in the water, the parent substances of these elements would be present, either in quantities corresponding to radioactive

equilibrium, or in amounts approximating it. It follows that we have to study the geochemistry of the radioactive elements—ionium, thorium and radiothorium—together with the geochemistry of radium and its isotopes.

The results of the radioactive analysis of the mineral springs cited above, as well as the method of analysis described, are naturally based on the chemical properties of these elements or on their place in the periodic system. Therefore, the genetic relation of these elements is given in figure 1 along with the weight proportions when in radioactive equilibrium.

We have studied the content of the radioactive elements, radium, mesothorium I, thorium X, and radiothorium, in mineral springs in the four watering places which are united under the title of mineral waters in North Caucasus.[1]

In this paper we will treat only the contents of radioactive elements in the spring waters of Gelesnovodsk, North Caucasus, and in the water of

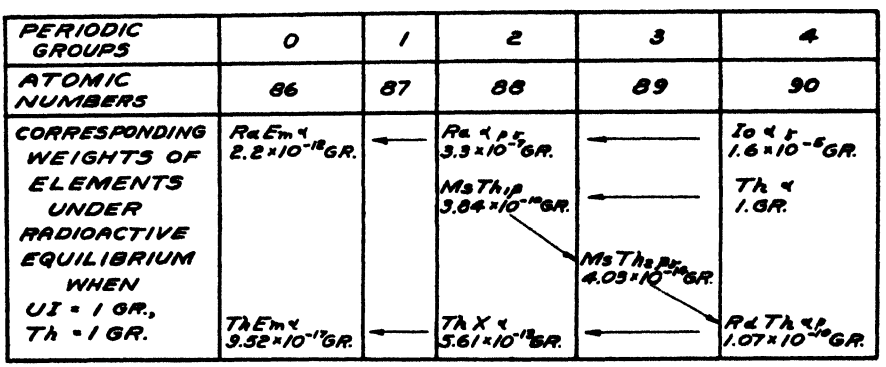

FIG. 1. GENETIC RELATION OF RADIOACTIVE ELEMENTS AND WEIGHT PROPORTIONS WHEN IN RADIOACTIVE EQUILIBRIUM

the pit-hole of the petroleum district of Uchta, North European Russia (see tables 3, 4, 5).

The method of analysis of the mineral water is as follows: 6 liters of water were taken for the analysis in the case of high concentrations of the radioactive elements (from 10^{-9} g. of radium to 10^{-11} g. of radium per liter). If the content of active elements was not large (from 10^{-11} g. of radium to 10^{-12} g. of radium per liter), 20 to 40 liters of water were taken.

A. First, barium carbonate was added, then the water was warmed to 80°C. on the steam bath and while being stirred, was acidified very slowly by hydrochloric acid until weakly acid. Thereby, if the water contained SO_4^{--} ions, barium and radium were precipitated; if the water was free from SO_4^{--} ions, sulfuric acid was added very slowly, for the complete

[1] These watering places are Kislovodsk, Essentuky, Pyatigorsk, and Gelesnovodsk, situated in the northern part of the Caucasus.

precipitation of barium and radium sulfates. In this way, one precipitation was sufficient to separate all of the radium and all of its isotopes from the water. Moreover, it was found that it was not necessary to add to the water a large excess of barium. It was quite sufficient to add from 0.5 g. to 0.4 g. of barium carbonate per liter of mineral water independent of the quantity of SO_4^{--} ions. By this method we received a small quantity of barium–radium sulfates and their slow conversion into chlorides was facilitated.

Nevertheless, barium chloride was added to the water for a control, and the process of precipitation of barium sulfate was performed a second time during the period of twenty-four hours.

B. The first and the second portions of barium–radium sulfate were separately transformed into chlorides. The solutions were then poured into standardized volumetric vessels.

C. Thorium X was measured by the emanation method by means of special equipment for that purpose. After that the vessel with the solution was sealed and put away for four to ten days for the accumulation of radium emanation (18). After the accumulation of the emanation, the measurement of radium was made by the same emanation method. For this measurement unifilar and bifilar electrometers were used, depending on the concentrations of active elements. The equipment was calibrated with standard solutions of radium and thorium X. After the measurement of radium, thorium X was measured again, then the measurement of radium was repeated. In this way a curve of decay of thorium X was obtained which gave the right quantity of thorium X and which checked the completeness of separation of thorium X from radiothorium.

D. After the decay of thorium X the vessel was put away for several months, for the accumulation of radiothorium from mesothorium I. Then the curve of the accumulation of radiothorium was measured by the emanation method once a month, and from this curve the content of mesothorium I was calculated.

E. After the elimination of radium and its isotopes from the water, the same sample of water was taken for the determination of thorium isotopes (ionium and radiothorium). Ferric chloride was added to the water and ferric hydroxide precipitated with ammonia. The ferric hydroxide was filtered, dissolved in hydrochloric acid, and then put into a standardized volumetric vessel. The solution was immediately measured by the emanation method in order to be certain of the absence of thorium X and radium. After that, the solution was put away for one month for the accumulation of thorium X from radiothorium. The curve of decay of radiothorium was measured and the quantity of radiothorium was calculated.

The results of analysis of the spring waters of Gelesnovodsk and of the pit-hole in the petroleum district of Uchta show that the radiothorium in

TABLE 3

*Watering place—Gelesnovodsk**

	SPRING SLAVYANOVSKY	SPRING NO. 1	SPRING SEMASHKO
Temperature of water on the surface (°C.)	55.5	44 0	55 0
1. Active elements in grams per liter of mineral water:			
Radium	$2\ 2 \times 10^{-10}$	$0\ 52 \times 10^{-10}$	$0\ 60 \times 10^{-10}$
Thorium X	$4\ 37 \times 10^{-5}$ (Th-unit†)	$26\ 8 \times 10^{-5}$ (Th-unit)	$32\ 3 \times 10^{-5}$ (Th-unit)
Mesothorium I	$3\ 65 \times 10^{-5}$ (Th-unit)	$19\ 5 \times 10^{-5}$	29.8×10^{-5} (Th-unit)
Radiothorium less than	5×10^{-6}	5×10^{-6}	5×10^{-6}
2. Other ions in grams per liter of mineral water:			
SO_4^{--}	0 8611	0 7602	0 7485
Cl^-	0 2898	0 2378	0 2506
HCO_3^-	1.3270	1 1956	1.1956
K^+	0 0364	0 0362	0 0338
Na^+	0 6369	0 5392	0 5517
Mg^{++}	0 0502	0 0477	0 0422
Ca^{++}	0 3035	0 2728	0 2755
Fe^{++}	0 0021	—	—
Dry residue	2 8850	2 5426	2 5470

* The watering place Gelesnovodsk is situated on the slopes of the mountain Gelesnaya. The water of these springs passes through eruptive rocks (Trachytes).

† In all calculations thorium X and mesothorium I are given in grams of thorium in radioactive equilibrium with the measured quantity of thorium X. This is designated (Th-unit). Owing to this designation, the calculation of decay and of rising is simplified. The standard solution was used for all measurements containing thorium, mesothorium I, radiothorium, and thorium X in equilibrium.

TABLE 4

Watering place—Gelesnovodsk (small springs)

NAME OF THE SPRINGS	TEMPERATURE OF THE SPRINGS	CONTENT OF RADIUM IN GRAMS PER LITER OF THE WATER
Nelubinsky	40 0	49×10^{-12}
Fransua	33 0	32×10^{-12}
Baryatinsky	19 0	Less than 3×10^{-12}
Neslobinsky	19 0	Less than 3×10^{-12}
Muravyewsky	17 0	Less than 1×10^{-12}

the water is undoubtedly not present in radioactive equilibrium with mesothorium I and thorium X. Moreover, the quantity of radiothorium in the water could not be determined in spite of applying the more sensitive unifilar electrometers for the measurement. The above-mentioned calculation of the contents of radiothorium in these spring waters must be considered as the limit of exact measurement.[2]

In spite of the absence of radioactive equilibrium in the thorium disintegration products, the data which were given show that in case any water increases its radium concentration, we may expect the concentration of mesothorium I and thorium X in the same water to increase also.

The amount of SO_4^{--} ions in the water is not an indication of the presence or absence of radium and its isotopes, but a higher temperature of the water at the surface of any spring which belongs to the group of active springs makes possible a greater content of radioactive elements.

THE PROCESS OF PRECIPITATION OF RADIUM FROM THE WATER OF MINERAL SPRINGS INTO THE SEDIMENTS

It is known that mineral springs deposit sediments and that these sediments contain radioactive elements if the water contains them. It would be very interesting to know under what conditions the separation of radium from the water takes place and in what compounds radium appears. Are there only radiobarites in nature or are there also other radium minerals without uranium? It has been possible to solve this problem by investigating the sediments of springs.

First, we were successful in showing one very important fact, namely, that the separation of radium from the water into the sediment does not depend on the presence of carbonate or sulfate ions in the water. Furthermore, it was found that the increase of radium in the sediments was greater when more ferric oxide was present, even in the case of the total absence of SO_4^{--} ions and HCO_3^- ions in the mineral water. To demonstrate this fact the following examples are given.

I. The sediments that are deposited by the water of the springs in Pyatigorsk consist mainly of calcium carbonate. These sediments are colored light yellow to brown by ferric hydroxide, according to the amount of ferric hydroxide present. The quantity of radium in the deposit is also

[2] The quantity of radiothorium in a liter of the water, 5×10^{-6}g. (Th-unit), is equal to 5.35×10^{-16} g. of radiothorium; 4.76×10^{-22}g. of thorium emanation corresponds to the quantity of radiothorium at radioactive equilibrium. In the precipitation of radiothorium from 20 liters of the water, the quantity of the whole measured emanation is equal to 9.52×10^{-21} g. of thorium emanation or 26 atoms. It is possible to determine radiothorium by the emanation method even if the amount per liter of water is less than 5×10^{-6} g. (Th-unit). In this case it would be necessary to have larger and more complicated equipment to operate with larger volumes of water.

dependent upon the amount of ferric oxide. This is shown by the following data given in terms of grams per 100 g. of sediment.

	DEPOSIT 1	DEPOSIT 2	DEPOSIT 3	DEPOSIT 4
	grams	*grams*	*grams*	*grams*
Ra	3×10^{-10}	10×10^{-10}	59×10^{-10}	111×10^{-10}
Fe_2O_3	0.05	0.18	1.07	1.83

II. The spring of the pit-hole "Kasennaya No. 1," in the petroleum district of Uchta in the North of Russia, contains 7.4×10^{-9} g. of radium per liter of water. This spring does not contain sulfate ions, as was mentioned

TABLE 5

*The pit-hole "Kasennaya No. 1" of the petroleum district Uchta**

THE CHEMICAL ELEMENTS	THE CONTENT IN GRAMS PER LITER OF MINERAL WATER
1. Active elements:	
Radium	$7\ 4 \times 10^{-9}$
Thorium X	$3\ 2 \times 10^{-2}$
Mesothorium I	$5\ 3 \times 10^{-2}$
Radiothorium	$2\ 0 \times 10^{-3}$
2. Other constituents:	
NaCl	49 5
SO_4^{--}	—
Fe^{++}	0 0252
Ca^{++}, Mg^{++}, SiO_2	Traces

* The pit-hole "Kasennaya No. 1," of the petroleum district Uchta, passes through sedimentary rocks. Their chemical composition and their content of radioactive elements were not investigated.

above. The sediment which is deposited at the surface contains 80.27 g. of ferric oxide and 40.8×10^{-8} gm. of radium per 100 g. of the deposit. From this it follows that the amount of adsorption of radium on ferric hydroxide under natural conditions can be calculated. 0.51×10^{-8} g. of radium corresponds to 1 g. of ferric oxide in the deposit. 20.82×10^{-8} g. of radium corresponds to 1 g. of ferric oxide in the water of the spring, in the form of ferrous iron.

So we see that 1 gram of ferric oxide which is precipitated adsorbs 2.44 per cent of the radium from the water.

III. The springs of the watering place of Gelesnovodsk contain 2.21×10^{-10} g. of radium per liter of water. The deposit is principally calcium

carbonate. Other constituents per 100 g. are Fe_2O_3, 7.78 g.; Al_2O_3, 0.88 g.; BaO and SrO, traces; Ra, 7.67×10^{-8} g.

The sediments of both this spring and the previous one contain mesothorium I and radiothorium, the latter in less than radioactive equilibrium with the mesothorium I.

We can calculate the adsorption of radium on the hydroxides of the trivalent metals. Thus, we find that 1 g. of trivalent metals which precipitates adsorbs 13.38 per cent of the radium from the water.

IV. The sediments from the mineral springs of Pyatigorsk contain, in addition to the oxides mentioned above, a small quantity of manganese dioxide. The amount of radium in the sediment increases as the amount

TABLE 6

Action of adsorbents on Slavyanovsky spring water*

CONDITIONS OF THE EXPERIMENT	NUMBER OF EXPERIMENTS MADE WITH THE WATER	QUANTITY OF RADIUM PER LITER OF WATER AFTER THE EXPERIMENT	PER CENT OF RADIUM ADSORBED FROM THE WATER
A. Filtration through barium without penetration of air	1	218×10^{-12}	1 4
	2	180×10^{-12}	16 6
	3	173×10^{-12}	21 7
B. Air was blown through the water and the resulting precipitate of ferric hydroxide was filtered	1	107×10^{-12}	51 6
	2	73×10^{-12}	67 0
	3	35×10^{-12}	84 1
C. The water after having had air blown through it was filtered through a layer of ferric hydroxide	1	20×10^{-12}	91 0
	2	7×10^{-12}	96 8
	3	6×10^{-12}	97 3

* The water of the Slavyanovsky mineral spring (Gelesnovodsk) contains 2.21×10^{-10} g. of radium per liter.

of manganese dioxide increases. For example: (1) The brown sediment contains per 100 g. 47.85 g. of ferric oxide, 1.79 g. of manganese dioxide, and 6.22×10^{-8} g. of radium; (2) the black sediment contains per 100 g. 21.37 g. of ferric oxide, 33.24 g. of manganese dioxide, and 49.50×10^{-8} g. of radium. Also, 1 g. of manganese dioxide bears 1.43×10^{-8} g. of radium and 1 g. of ferric oxide bears 7.6×10^{-10} g. of radium.

Therefore, analyzing the sediments of the same spring, it was found that it was possible to calculate the amount of radium in the sediments if the quantities of ferric oxide and manganese dioxide were known. On the other hand, it was possible to calculate the amount of manganese dioxide in the sediment if the amount of radium and ferric oxide was determined. From this we can see that the natural separation of radium and its isotopes from the water of mineral springs is a very common process.

The quantity of radium in a deposit does not depend on the sulfates contained in the sediment, but depends on the quantity of ferric and manganese oxides in it. The per cent of radium adsorbed by the hydroxides deposited in the sediment varies among springs but has a characteristic value for each spring.

It is a very interesting question whether radium contained in active barites (so-called radiobarites) is a product of isomorphous crystallization of barium–radium sulfate, or whether radium in active barites arose from ionium. Radiobarites, according to all descriptions, contain ferric oxide, and they are yellow in color. As the age of some active barites must be more than the average life of radium, we are obliged to suppose ionium precipitated from solution with iron when the barites crystallized (8).

The water of the Slavyanovsky spring (Gelesnovodsk) was passed through several adsorbents. When the water had passed through barium sulfate, the radium was not adsorbed by the sulfate in noticeable quantities. If air was blown into the water and ferrous iron was oxidized, radium with ferric hydroxide was precipitated from the water. But the best results were obtained when the water, after having air blown through it, was passed through a layer of hydroxides. The quantities of the radium precipitated from the water are shown in table 6.

DISCUSSION OF RESULTS

From the studies of concentration of radium, thorium, and their isotopes in the water of natural springs, we can see that there is no radioactive equilibrium between the active elements. This result was to be expected, because near a pH of 7 the elements thorium, ionium, radiothorium, etc., must be in colloidal form or conglomerate accumulations and cannot exist in the form of ions (2, 3, 6, 19). The elements radiothorium, ionium, etc., if they are in a colloidal or conglomerate condition, precipitate from the water onto the surface of the rocks more easily than radium. The high concentration of radium and of its isotopes in comparison to that of their parent substances in the analyzed water of springs, shows us without question that radium, thorium X, and mesothorium I do not immediately rise in the water, but are extracted from the rocks. The nature of the rocks which yield radium in the water is quite well-known in some cases, for example, the water of the springs of Gelesnovodsk flows through trachyte before reaching the surface.

The trachytes were analyzed for radium, which was found to range from 5×10^{-12} g. of radium to 13×10^{-12} g. of radium per gram of rock.

Experiments made on the trachytes of Gelesnovodsk and Pyatigorsk have shown that radium passes easily into acidified water. Five liters of water without radium were warmed with 200 g. of trachyte for twenty hours at a

temperature of 55°C. The following amounts of radium were found in the water: (a) 40×10^{-12} g., (b) 95×10^{-12} g., and (c) 127×10^{-12} g.

From the whole investigation we see that radium and its isotopes are quite movable elements in the upper parts of the solid crust.

In the geochemical process—*rocks* → *mineral springs* → *sediments on the surface*—we have a thousandfold increase of the concentration of radium.

Since radium is concentrated by ferric and manganous hydroxides, these might be regarded as new kinds of active minerals.

SUMMARY

1. High concentrations of radium and mesothorium I in natural waters are described. The highest concentrations of these elements, which amount to 1.8×10^{-8} g. of radium and 2×10^{-2} g. of mesothorium I (Th-units) per liter of water, have been found in salt water associated with petroleum beds.

2. A method of simultaneous determination of radium, mesothorium I, thorium X, and radiothorium is described.

3. It has been found that the presence of sulfate ions does not effect this high concentration of radium or mesothorium I in natural water.

4. The amount of radiothorium in natural active water was found to be less than that required for radioactive equilibrium with the mesothorium I which was present in this water.

5. A study of the process of migration of radium in nature has shown that radium and mesothorium I are easily transferred from eruptive rocks to mineral waters and from mineral waters to sediments in such a manner that the concentration of radium in sediments is increased a thousand times.

6. Precipitation of radium and mesothorium from water is associated with manganese and ferric hydroxides in sediments.

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STUDIES OF CELLS WITH LIQUID-LIQUID JUNCTIONS. V

STANDARDS FOR HYDROGEN ION MEASUREMENTS AND THE SECOND DISSOCIATION CONSTANT OF PHOSPHORIC ACID

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I. INTRODUCTION

A common type of cell used in the electrometric determination of hydrogen ions is the following:

$$\text{Hg} \mid \text{HgCl}, 0\ 1\ N\ \text{KCl} \mid 3.5\ N\ \text{KCl} \mid \text{solution S} \mid \text{H}_2 \tag{1}$$

The exact thermodynamic treatment of such cells has been discussed in a previous paper (6). The electromotive force is a definite but rather complicated function of the concentrations and transport numbers of all the ionic species and of the mean activity coefficients of all the electrolytes present, not only in the electrode solutions and the bridge solution but also in the transition layers between. The formulas, though thermodynamically exact, are of little practical use. To use them it would be necessary first to make measurements with a large (theoretically infinite) number of cells without liquid-liquid junctions in order to obtain the required values of mean activity coefficients, not to mention the required knowledge of transport numbers.

It is therefore expedient to use the formula

$$E = E_0 + E_D + \frac{RT}{F} \log C_{\text{H}^+} f_{\text{H}^+} \tag{2}$$

where E is the electromotive force of the cell, E_0 is a constant, E_D is the ideal value for the diffusion potentials for the whole cell, and C_{H^+} is the concentration of hydrogen ion in the solution S, and f_{H^+} may be called the activity coefficient of the hydrogen ion in the solution S. This formula is actually a conventional definition of E_0 and of f_{H^+}, the value of either depending on the value conventionally assigned to the other. However as long as the solution S is so dilute that the activity coefficient has approximately the same value for various electrolytes of the same electric type, and as long as the solution S contains only small concentrations of either hydrogen ion or hydroxyl ion, it is possible to assign to E_0 a value such

that the value of f_{H^+} defined and measured according to equation 2 will to within a few units per cent be equal to that of $f_{\pm}$, the mean activity coefficient of a uni-univalent electrolyte in solution S. It is only to this approximation that there is any sense in regarding the activity coefficient f_{H^+} measured by such a cell as a thermodynamic quantity. Even at dilutions so great that the activity coefficients, $f_{\pm}$, of all uni-univalent electrolytes have the same value to within one per cent or less, it is possible for f_{H^+} to differ by as much as three or four per cent from $f_{\pm}$ of uni-univalent electrolytes. For this reason there does not seem to be much sense in determining values of $-\log C_{H^+} f_{H^+}$, or paH[1] as it is usually denoted, to a greater accuracy than 0.01, or at the most 0.005.

If the liquid–liquid junctions are made in a suitable manner (7, 9, 16, 19) the electromotive forces of these cells are about as reproducible and stable as most cells without such junctions and the value of E_D may be calculated by using Henderson's formula (12).

Bjerrum and Unmack (3) have made extensive measurements of cells of type 1 and have used formula 2 in their computations. The treatment of our own data is in principle the same as that of Bjerrum and Unmack. We wish however to draw attention to a few differences of detail.

First in computing E_D by the use of Henderson's formula, Bjerrum and Unmack use the value 0.497 for the transport number t_{K^+} of the potassium ion in potassium chloride. They discuss in some detail how their computations would be affected by the choice of a different value. Meanwhile accurate determinations of this quantity at 25°C. have been made by Longsworth (13) and by MacInnes and Dole (15). According to their measurements this transport number has the constant value 0.490 at all concentrations up to half molar. As most of the contribution to E_D comes from the more dilute end of the transition layer, we have used this value for t_{K^+}. Our values of E_D therefore differ somewhat from those of Bjerrum and Unmack. For the ions in the more dilute solutions S, the ionic conductivities require to be known only roughly.

Second, we do not believe there is anything to be gained in attempting to compute either f_{H^+} or related quantities with an accuracy greater than corresponds to the difference between the mean activity coefficients of two uni-univalent electrolytes.

Third, whilst in entire agreement with Bjerrum and Unmack as regards the principle to be used in choosing the best value for E_0, we make a different choice of solutions to which we attach most weight.

II. MEASUREMENTS

All the cells measured were of the type 1, the composition of the solution S being one of those given in table 1 and the temperature being 25°C.

[1] paH is a conventionalized form of pa_H.

The solutions were prepared and standardized as described in the following paper (8). The experimental set-up was in all essential respects that used by Unmack and Guggenheim (19). In particular the junction was made by dipping the side-tube of the hydrogen electrode vessel into a U-tube containing 3.5 molar potassium chloride. The levels of the solutions in the U-tube and the electrode vessel were so adjusted that on opening the stopcock between the electrode and the side tube the liquid from the U-tube always slowly flowed about halfway up the side tube. The electromotive force reached a constant value usually within half an hour. This was reproducible within at least a tenth of a millivolt and stable for at least a day. Four calomel electrodes were prepared and these checked within 0.1 millivolt.

TABLE 1

Hg | HgCl, 0.1 *M* KCl | 3.5 *M* KCl | solution S | H_2 *at 25°C.*

COMPOSITION OF SOLUTION S			TOTAL IONIC STRENGTH	E. M. F. MEASUREMENTS*		paH
Acid constituent	Basic constituent	Neutral salt		Our values	Values determined by Bjerrum and Unmack	
moles per liter	*moles per liter*	*moles per liter*		*mv.*	*mv.*	
(a) 0 01 HCl		0 09 KCl	0 10	−458 30	−458 40	2 10
(b) 0 10 HCl			0 10	−400 80	−400 90	1 07
(c) 0 01 HAc	0 01 NaAc		0 01	−613 90		4 80
(d) 0 01 HAc	0 01 NaAc	0 09 KCl	0 10	−609 75		4 67
(e) 0 10 HAc	0 10 NaAc		0 10	−610 10		4 66
(f) 0 0025 NaH_2PO_4	0 0025 Na_2HPO_4	0 00242 NaCl	0 0125	−753 40	−753 10	7 07
(g) 0 025 NaH_2PO_4	0 025 Na_2HPO_4	0 0242 NaCl	0 125	−738 60	−738 20	6 835
(h) 0 050 NaH_2PO_4	0 050 Na_2HPO_4	0 0485 NaCl	0 250	−732 45		6 735

* Positive value of E means that electrode on right is positive (American convention).

The results of our measurements are recorded in table 1. The first four columns give the composition of the hydrogen electrode solution S. The fifth column gives the measured electromotive force corrected to the mean value of the calomel electrodes and to a hydrogen pressure of one atmosphere. The sixth column gives some electromotive force values of Bjerrum and Unmack (3), which agree fairly satisfactorily with our values. The last column will be discussed in the next section.

III. CHOICE OF E_0

The value of E_0 originally proposed by Sörensen was based on a misinterpretation of conductivity data at a time when it was believed that solutions of electrolytes obey the ideal laws. It is now generally agreed

and admitted by Sörensen (18) that this value of −337.6 millivolts at 25°C. is not the most desirable. Various authors have suggested other values and some of these are discussed at length by Clark (4). But there has been a natural reluctance to adopt any other value until one could be chosen likely to be strongly established and permanent. Güntelberg and Schiödt (10) discuss the unfortunate confusion due to the continued use of the obsolete Sörensen value and estimate that values of paH or $-\log_{10} C_{H^+} f_{H^+}$ calculated from the Sörensen value are too low by 0.05 ± 0.015, but they agree that an alternative standard value should not be adopted until it could be fixed to within 0.01 in paH. We wish to put forward what we believe to be a strong case for the adoption of the value

$$E_0 = -333.7 \text{ millivolts at } 25°\text{C.}$$

according to which the Sörensen values of pH, assuming the computation of E_D has been correctly carried out, will be too low by 0.065. We shall show that for the five solutions (a) 0.01 *M* hydrochloric acid + 0.09 *M* potassium chloride, (b) 0.10 *M* hydrochloric acid, (c) 0.01 *M* acetic acid + 0.01 *M* sodium acetate, (d) 0.01 *M* acetic acid + 0.01 *M* sodium acetate + 0.09 *M* potassium chloride, and (e) 0.10 *M* acetic acid + 0.10 *M* sodium acetate, this value of E_0 leads to most reasonable values of f_{H^+} and f_{Ac^-}.

Solutions a and b have often before been suggested as standards. One of the objections raised against the use of solution b is the difficulty of obtaining definite values for E owing to the large diffusion potential. Actually there is no difficulty in obtaining reproducible and stable values if the junction is made in the correct manner. Solutions c, d, and e have become suitable for standards only quite recently, thanks to the accurate determination of the dissociation constant of acetic acid by Harned and Ehlers (11), who used cells without any liquid–liquid junctions.

Let us first consider cells made in the solutions a and b. In both these the value of C_{H^+} is known, being equal to the stoichiometric concentration of hydrochloric acid. According to the best values of the universal contants compiled by Birge (1) the value of $\frac{RT}{F} \log_e 10$ at 25°C. is 59.151 international millivolts. We therefore have, according to equation 2,

$$59.15 \log_{10} f_{H^+} = E - E_0 - E_D - 59.15 \log_{10} C_{H^+} \tag{3}$$

Inserting the numerical values of E, E_0, and E_D we obtain for cell a

$$59.15 \log_{10} f_{H^+} = -458.3 + 333.7 + 0.4 + 118.3 = -5.9$$

and for cell b

$$59.15 \log_{10} f_{H^+} = -400.8 + 333.7 + 3.64 + 59.15 = -4.3$$

The corresponding values of f_{H^+} are 0.795 in solution a and 0.85 in solution b.

An entirely different convention sometimes used (14, 17) for assigning values to ionic activity coefficients is to set the activity coefficient f_{Cl^-} of the chloride ion in both solutions a and b equal to the value 0.76 of the mean activity f_{KCl} of potassium chloride in 0.10 M potassium chloride. This convention leads to values of f_{H^+} equal to 0.80 in solution a and 0.84 in solution b. The agreement between these values and those obtained by the use of our value of E_0 is extremely satisfactory.

Let us now consider the three acetate buffers c, d, and e. Since each buffer contains equal concentrations of acetic acid and sodium acetate, we have, according to equation 2,

$$E = E_0 + E_D + \frac{RT}{F} \log_e K_{HAc} - \frac{RT}{F} \log_e \frac{f_{Ac^-}}{f_{HAc}} \tag{4}$$

where K_{HAc} is the thermodynamic dissociation constant of acetic acid. Its value determined by Harned and Ehlers is 1.75×10^{-5} at 25°C. From the experimental value of E and the known values of E_0, E_D, and K_{HAc}, we are able to calculate f_{Ac^-}/f_{HAc}. The computations are shown in table 2. If we ignore the deviation of f_{HAc} from unity, then we obtain the values of f_{Ac^-} given in the last row of the table. It is to be noted that the value 0.90 for f_{Ac} at the ionic strength 0.01 is exactly equal to $f_{\pm}$ for any typical uni-univalent electrolyte at the same ionic strength. Moreover the values 0.80 and 0.81 of f_{Ac} at the ionic strength 0.10 are within the range of values of the mean activity coefficients of typical uni-univalent electrolytes at the same ionic strength.

We see then that the value we suggest for E_0 leads to eminently reasonable values for f_{H^+} in the solutions a and b, and equally reasonable values for f_{Ac} in the solutions c, d, and e. The corresponding values for $-\log_{10} C_H \cdot f_{H^+}$ or paH for all five solutions are given in the last column of table 1.

The rather large discrepancy between the value −333.7 which we have chosen for E_0 and the value −336.0 selected by Bjerrum and Unmack is due partly to their use of the value $t_{K^+} = 0.497$ in potassium chloride and partly to their attaching greater weight to much more dilute solutions of hydrogen chloride, where the experimental uncertainty is likely to be great. Even if the experimental values at these high dilutions are reliable, it seems to us preferable to choose for E_0 a value which leads to reasonable values of f_{H^+} and f_{Ac^-} in solutions of concentrations in the more generally useful range of 0.01 M to 0.1 M.

It should not be necessary to mention that in order to obtain the best results it is essential not to ignore E_D. Whereas its value is usually not more than about one millivolt, there seems to be a surprisingly widespread belief that it is vanishingly small. In the case of measurements on protein solutions and the like, where it is not possible to calculate E_D, one can ob-

tain a rough estimate of its magnitude by the procedure proposed by Bjerrum (2), of comparing the values of E obtained by using as bridge solution first 3.5 M potassium chloride and second 1.75 M potassium chloride. Bjerrum and Unmack (reference 3, p. 50) give an emphatic warning against exaggerated ideas of the reliability of this procedure. It is to be recommended only when it is not possible to calculate E_D.

TABLE 2

Hg | HgCl, 0.1 M KCl | 3.5 M KCl | solution S | H_2 *at 25°C.*

	c	d	e
Composition of solutions S	0 01 NaAc 0.01 HAc	0 01 NaAc 0.01 HAc 0 09 KCl	0.10 NaAc 0 10 HAc
E	−613 9	−609.75	−610.1
E_D *	+1 85 −3 33 −1.48	+1 85 −1 85 0 00	+1.85 −2 46 −0 60
$E - E_D$	−612 42	−609 75	−609 5
E_0	−333.7	−333.7	−333 7
$E - E_D - E_0 = \frac{RT}{F}\log_e C_{H^+}f_{H^+}$	−278.7	−276 05	−275.8
$\frac{RT}{F}\log_e K_{HAc}$	−281 4	−281 4	−281 4
$-\frac{RT}{F}\log_e f_{Ac^-}$	+2.7	+5.35	+5 6
$\log_{10} f_{Ac^-}$	−0.045	−0.090	−0 095
f_{Ac^-}	0 90	0.81	0.80
$\text{paH} = -\log_{10} C_{H^+}f_{H^+}$	4 80	4 67	4 66

* The value +1.85 given first represents the contribution of the junction 0 1 M KCl | 3.5 M KCl. The value given next is the contribution of the junction 3.5 M KCl | solution S. The third value, representing E_D for the whole cell, is the algebraic sum of the first two.

IV. SECOND DISSOCIATION CONSTANT OF PHOSPHORIC ACID

Having chosen a value for E_0 we use our electrometric measurements in the phosphate buffers f, g, and h to compute values of $C_{H^+}f_{H^+}$ by exactly the procedure used by Bjerrum and Unmack. As the ratio $C_{HPO_4^{--}}/C_{H_2PO_4^-}$ is unity in each case, the thermodynamic dissociation constant $K_{H_2PO_4^-}$ is given by

$$K_{H_2PO_4^-} = \frac{C_{H^+}\cdot C_{HPO_4^{--}}}{C_{H_2PO_4^-}}\cdot\frac{f_{H^+}\cdot f_{HPO_4^{--}}}{f_{H_2PO_4^-}} = C_{H^+}f_{H^+}\cdot\frac{f_{HPO_4^{--}}}{f_{H_2PO_4^-}} \tag{5}$$

As already mentioned it is possible to compute such a quantity as $K_{H_2PO_4^-}$ from measurements of cells with liquid–liquid junctions only with an accuracy that ignores specific differences between the activity coefficients of two electrolytes of the same type. In a paper to be published shortly it will be pointed out that the activity coefficients of numerous electrolytes of all valence types are correctly given within a few units per cent up to an ionic strength of 0.1, if the activity coefficient of each ion of valency Z is calculated according to

$$-\log_{10} f = 0.50\, Z^2 \frac{\sqrt{\Gamma}}{1+\sqrt{\Gamma}} \tag{6}$$

where Γ is the total ionic strength of the solution. This formula is of the Debye-Hückel (5) type in which the parameter a, the "mean ionic diameter" is set equal to 3.0 A.U. According to this formula we have

$$\log_{10} \frac{f_{HPO_4^{--}}}{f_{H_2PO_4^-}} = -1.50 \frac{\sqrt{\Gamma}}{1+\sqrt{\Gamma}} \tag{7}$$

Combining the values of $f_{HPO_4^{--}}/f_{H_2PO_4^-}$ thus calculated with the values of $C_H \cdot f_{H^+}$ obtained from the electrometric measurements we are able to obtain values of $K_{H_2PO_4^-}$. The complete computations are given in table 3. The three independent values obtained for $K_{H_2PO_4^-}$ agree remarkably well. As the formula (7) for activity coefficients is not expected to be accurate at an ionic strength as high as 0.25, the agreement of the value of $K_{H_2PO_4^-}$ given by the third solution with those given by the other two is probably fortuitous. Taking the mean of the values given by the two most dilute solutions we obtain as the value of $K_{H_2PO_4^-}$, 5.97×10^{-8} with an estimated accuracy of 2 or 3 per cent. The value estimated by Bjerrum and Unmack (reference 3, p. 132) was 6.20×10^{-8}.

V. VALUES FOR E_0 AT OTHER TEMPERATURES

As already pointed out by Bjerrum and Unmack the selection of the most likely value for E_0 depends on the value assumed for t_{K^+} in potassium chloride. This uncertainty is however pronounced only in very dilute solutions. If then we choose standard solutions of total concentration 0.10 M we may without serious error assume that t_{K^+} in potassium chloride has the same value, 0.490, at other temperatures as at 25°C. On this basis and using Bjerrum and Unmack's measurements we come to the conclusion that the most reasonable values of E_0 at the various temperatures of their measurements are those given in table 4. We believe that these values are definite to within about one quarter of a millivolt, that is to within 0.005 of a pH unit or within 1 per cent in f_{H^+}. In the same table are given the values of f_{H^+} in three standard solutions corresponding to this choice of E_0

and also the values of f_{H^+} calculated on the convention of setting f_{Cl^-} equal to f_{KCl} in 0.1 M potassium chloride. The agreement between the two independent conventions is most satisfactory.

TABLE 3

Hg | HgCl, 0.1 M KCl | 3.5 M KCl | solution S | H_2 *at 25°C.*

	f	g	h
Composition of solutions S. . . .	0 01 Na^+ 0.0025 $H_2PO_4^-$ 0 0025 HPO_4^{--} 0 0025 Cl^-	0.10 Na^+ 0.025 $H_2PO_4^-$ 0 025 HPO_4^{--} 0 025 Cl^-	0.20 Na^+ 0 05 $H_2PO_4^-$ 0.05 HPO_4^{--} 0.05 Cl^-
Ionic strength Γ.	0 0125	0.125	0.25
$\sqrt{\Gamma}$.	0 112	0.353	0.50
E.	−753 4	−738 6	−732.45
E_D*	+1.85 −3 24 −1 40	+1.85 −2.35 −0 50	+1.85 −2 21 −0.35
$E - E_D$.	−752 0	−738 1	−732.1
E_0.	−333.7	−333.7	−333 7
$E - E_D - E_0$.	−418.3	−404 4	−398 4
paH = $-\log_{10} C_{H^+} f_{H^+}$.	7 072	6.837	6.735
$C_{H^+} f_{H^+}$.	0 847 × 10^{-7}	1.45 × 10^{-7}	1 84 × 10^{-7}
$-\log_{10} \frac{f_{H_2PO_4^-}}{f_{HPO_4^{--}}}$.	0 151	0.391	0.500
$-\log_{10} K_{H_2PO^{4-}}$.	7.222	7 226	7.235
$K_{H_2PO_4^-}$.	6 00 × 10^{-8}	5.94 × 10^{-8}	5.82 × 10^{-8}

* The value +1.85 given first represents the contribution of the junction 0.1 M KCl | 3.5 M KCl. The value given next is the contribution of the junction 3.5 M KCl | solution S. The third value, representing E_D for the whole cell, is the algebraic sum of the first two.

TABLE 4

	TEMPERATURE				f_{H^+} ACCORDING TO CONVENTION $f_{Cl^-} = f_{KCl}$
	0°C.	18°C	25°C	37°C.	
E_0	−334.2	−334 2	−333.7	−332.7	
f_{H^+} in 0.01 M HCl + 0.09 M KCl . .	0 80	0.80	0.80	0.80	0.80
f_{H^+} in 0.01 M HCl + 0.09 M NaCl. .	0 83	0 82	0.82	0.82	0.82
f_{H^+} in 0.10 M HCl.		0 84	0.85	0 85	0.84

We are pleased to learn from Professor Bjerrum that he is in complete agreement with the contents of the present paper and that he accepts our E_0 value at 25°C. as the most reasonable one to use on the available experimental material.

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SALT EFFECTS ON SULFONPHTHALEIN INDICATORS[1]

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I. INDICATOR-BUFFER EQUILIBRIA

According to the terminology of Brönsted (3) the two forms of any indicator function respectively as an acid and as a base. Denoting the acid form by HI and the basic form by I there is an equilibrium of the form

$$HI \rightleftharpoons I + H^+ \tag{1}$$

The electric charge of the acid form HI may be positive, zero, or negative according to the nature of the indicator. The electric charge of the basic form I is of course algebraically one less than that of HI. Similarly a buffer solution may be regarded as a mixture of an acid HA and a base A which control the hydrogen ion concentration according to the equilibrium

$$HA \rightleftharpoons A + H^+ \tag{2}$$

The electric charge of the acid form HA may be positive, zero, or negative, while that of the basic form A is of course algebraically one less than that of HA.

The exact thermodynamic treatment of such equilibria was given by Brönsted (2) in 1921. Writing C for concentrations and f for activity coefficients the thermodynamic equilibrium conditions are

$$\frac{C_I \cdot C_{H^+}}{C_{HI}} = K_{(C)HI} = K_{HI} \cdot \frac{f_{HI}}{f_{H^+} f_I} \tag{3}$$

$$\frac{C_A \cdot C_{H^+}}{C_{HA}} = K_{(C)HA} = K_{HA} \cdot \frac{f_{HA}}{f_{H^+} f_A} \tag{4}$$

where K_{HI} is the thermodynamic acid constant of the indicator and K_{HA} that of the acid constituent of the buffer. For a given temperature and solvent K_{HI} and K_{HA} are true constants. The equilibrium concentrations products $K_{C(HI)}$ and $K_{C(HA)}$ on the other hand are not constants but depend on the concentration of electrolytes present.

[1] We wish to express our indebtedness to Mr. E. Güntelberg of Copenhagen for reading through the manuscript of this paper and pointing out to us certain inaccuracies in formulas 14 to 17 which we have since corrected.

In the same paper Brönsted pointed out that instead of the two equilibria 1 and 2 one may consider directly the double acid–base equilibrium between the indicator and the buffer

$$\mathrm{HI} + \mathrm{A} \rightleftharpoons \mathrm{I} + \mathrm{HA} \tag{5}$$

The thermodynamic equilibrium condition is

$$\frac{C_{\mathrm{I}} \cdot C_{\mathrm{HA}}}{C_{\mathrm{HI}} \cdot C_{\mathrm{A}}} = K_C = \frac{K_{(C)\mathrm{HI}}}{K_{(C)\mathrm{HA}}} = \frac{K_{\mathrm{HI}}}{K_{\mathrm{HA}}} \cdot \frac{f_{\mathrm{HI}} \cdot f_{\mathrm{A}}}{f_{\mathrm{I}} \cdot f_{\mathrm{HA}}} \tag{6}$$

Whereas $K_{\mathrm{HI}}/K_{\mathrm{HA}}$ is a true constant, the equilibrium concentrations product $K_{(C)\mathrm{HI}}/K_{(C)\mathrm{HA}}$ or K_C depends on the concentration of electrolytes present. If then one observes the color of an indicator present in small amount in a buffer solution, the value of $C_{\mathrm{HA}}/C_{\mathrm{A}}$ is known from the composition of the buffer and that of $C_{\mathrm{I}}/C_{\mathrm{HI}}$ is given by the color. We are therefore able to calculate the value of K_C. By determining this product at various salt concentrations and extrapolating to infinite dilution, one obtains a value of $K_{\mathrm{HI}}/K_{\mathrm{HA}}$; thence by division one obtains directly values of the product $f_{\mathrm{HI}} \cdot f_{\mathrm{A}}/f_{\mathrm{I}} \cdot f_{\mathrm{HA}}$. This product is a measure of the salt effect on the indicator buffer equilibrium 5. If the value of either K_{HI} or K_{HA} is known from previous determinations, then we can calculate the other from the known ratio $K_{\mathrm{HI}}/K_{\mathrm{HA}}$. If moreover we can rely on some formula to give the activity coefficients product $f_{\mathrm{H}^+} \cdot f_{\mathrm{A}}/f_{\mathrm{HA}}$ which measures the salt effect of the buffer equilibrium 2, we can from the known value of $f_{\mathrm{HI}} \cdot f_{\mathrm{A}}/f_{\mathrm{I}} \cdot f_{\mathrm{HA}}$ calculate the value of the product $f_{\mathrm{H}^+} \cdot f_{\mathrm{I}}/f_{\mathrm{HI}}$ which measures the salt effect of the equilibrium 1.

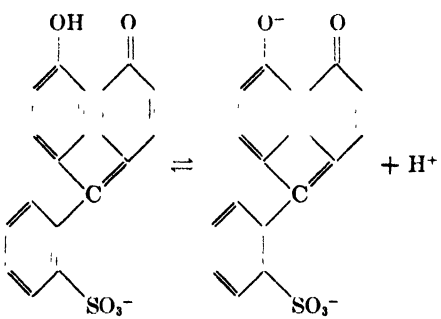
In discussing or measuring the salt effect on indicators it is more usual to consider the indicator equilibrium 1 rather than the indicator–buffer equilibrium 5 as we do. Other authors determine $C_{\mathrm{I}}/C_{\mathrm{HI}}$ from the color and attempt to estimate the value of $C_{\mathrm{H}^+} f_{\mathrm{H}^+}$ by electrometric measurements on cells with liquid–liquid junctions. A thermodynamic analysis of such measurements (6), however, shows that the quantity measured is not $C_{\mathrm{H}^+} f_{\mathrm{H}^+}$, but rather $C_{\mathrm{H}^+} f_?$, where $f_?$ is a complicated function of the mean activity coefficients of all the electrolytes and the transport numbers of all the ions present, not merely in the electrode solution but also in the bridge solution and at each part of the transition layer between the electrode solution and the bridge solution. Estimates based partly on experiment and partly on approximate computations (16) indicate that the confusion between $C_{\mathrm{H}^+} f_?$ and $C_{\mathrm{H}^+} f_{\mathrm{H}^+}$ in even quite dilute solutions may in some cases lead to inaccuracies of the order of 4 per cent in a concentration, or 1 millivolt in an E.M.F., or 0.015 on the pH scale. It is by no means certain that the error may not sometimes be twice as great as this estimate. Any computation of the salt effect on an indicator equilibrium which is dependent on electrometric measurements of cells with liquid junctions is therefore

likely to be uncertain by about 4 per cent. As it is possible to make colorimetric measurements with a higher accuracy than this, it seems to us preferable to make our determinations mainly independent of electrometric measurements.

Our criticism of the use of cells with liquid–liquid junctions does not apply to the measurements of Güntelberg and Schiödt (10), as they took care to make their liquid–liquid junction potentials negligibly small. Their procedure is however applicable only to comparatively concentrated salt solutions.

II. APPLICATION TO SULFONPHTHALEIN INDICATORS

Two indicators were used, both substitution derivatives of phenolsulfonphthalein. The various forms in which indicators of this type can exist have been discussed by Kolthoff (14). The only two forms which concern us are the derivatives of



I Yellow II Blue

Form I is the yellow acid form with a single negative charge, which we may refer to as HI^-, and form II is the blue basic form with a double negative charge, which we may refer to as I^{--}.

The buffers chosen for our investigation were of the types

$$H_2PO_4^- \rightleftharpoons HPO_4^{--} + H^+ \tag{7}$$

and

$$HAc \rightleftharpoons Ac^- + H^+ \tag{8}$$

where Ac denotes acetate. It was desirable in each case to use a sulfonphthalein indicator whose acid constituent was of strength comparable to that of the acid constituent of the buffer. The most suitable ones for this purpose are dibromothymolsulfonphthalein (bromothymol blue) in the primary–secondary phosphate buffer, and tetrabromo-*m*-cresolsulfon-

phthalein (bromocresol green) in the acetic acid–acetate buffer. The indicator–buffer equations for these combinations are

$$\mathrm{HAc} + \mathrm{I}^{--} \rightleftharpoons \mathrm{Ac}^{-} + \mathrm{HI}^{-} \tag{9}$$

$$\mathrm{H_2PO_4}^{-} + \mathrm{I}^{--} \rightleftharpoons \mathrm{HPO_4}^{--} + \mathrm{HI}^{-} \tag{10}$$

$$K_C = \frac{C_{\mathrm{I}^{--}}}{C_{\mathrm{HI}^{-}}} \cdot \frac{C_{\mathrm{HAc}}}{C_{\mathrm{Ac}^{-}}} = \frac{K_{\mathrm{HI}^{-}}}{K_{\mathrm{HAc}}} \cdot \frac{f_{\mathrm{HI}}\, f_{\mathrm{Ac}^{-}}}{f_{\mathrm{I}^{--}} f_{\mathrm{HAc}}} \tag{11}$$

$$K_C = \frac{C_{\mathrm{I}^{--}}}{C_{\mathrm{HI}}} \cdot \frac{C_{\mathrm{H_2PO_4}^{-}}}{C_{\mathrm{HPO_4}^{--}}} = \frac{K_{\mathrm{HI}}}{K_{\mathrm{H_2PO_4}^{-}}} \cdot \frac{f_{\mathrm{HI}}\, f_{\mathrm{HPO_4}^{--}}}{f_{\mathrm{I}^{--}} f_{\mathrm{H_2PO_4}^{-}}} \tag{12}$$

According to the theory of Debye and Hückel (5) the activity coefficients may be calculated according to the formula

$$-\log_{10} f_i = 0.50 \frac{Z_i^2\, \Gamma^{1/2}}{1 + 0.33 a \Gamma^{1/2}} \tag{13}$$

where f_i denotes the activity coefficient of the ion i of valency Z_i, Γ is the ionic strength, and a is a certain mean ionic diameter in A.U. of the given ion and other ions in the solution. A somewhat similar formula to formula 13 with certain advantages over it and equally applicable at ionic strengths up to 0.1 is the following (7)

$$-\log_{10} f_i = 0.50\, Z_i^2 \frac{\Gamma^{1/2}}{1 + \Gamma^{1/2}} + \sum_k B_{ik} C_k \tag{14}$$

in which the coefficient of $\Gamma^{\frac{1}{2}}$ in the denomination is given the value unity, the specific differences between various ions being taken care of by the term $\sum_k B_{ik} C_k$ where C_k denotes the concentration of the ionic species k; the quantities B_{ik} are constants, and the summation $\sum_k$ extends over all ionic species k of *opposite sign to that of the species i.*

Applying formula[1] 14 to the indicator–buffer equilibria, we obtain

$$-\log_{10} \frac{f_{\mathrm{HI}} \cdot f_{\mathrm{A}}}{f_{\mathrm{I}} \cdot f_{\mathrm{HA}}} = \frac{0.50\, \Gamma^{1/2}}{1 + \Gamma^{1/2}} (Z_{\mathrm{HI}}^2 + Z_{\mathrm{A}}^2 - Z_{\mathrm{I}}^2 - Z_{\mathrm{HA}}^2) + \sum_k B_{ik} C_k \tag{15}$$

where Z_{HI} denotes the valency of HI, and so on. In the particular case of the sulfonphthalein indicators and the sodium phosphate buffers used formula 15 becomes

$$-\log_{10} \frac{f_{\mathrm{HI}^{-}} \cdot f_{\mathrm{HPO_4}^{--}}}{f_{\mathrm{I}^{--}} \cdot f_{\mathrm{H_2PO_4}^{-}}} = B C_{\mathrm{Na}^{+}} \tag{16}$$

where B is a constant, the coefficient of the term in $\Gamma^{\frac{1}{2}}$ being zero. For the equilibrium between sulfonphthalein indicator and the sodium acetate buffer on the other hand formula 15 becomes

$$-\log_{10}\frac{f_{HI^-}\cdot f_{Ac^-}}{f_{I^{--}}\cdot f_{HAc}} = -1.0\frac{C^{1/2}}{1+C^{1/2}} + BC \tag{17}$$

the ionic strength in this case being the same as the concentration C of either sodium ion or acetate ion.

Thus in the phosphate buffers the salt effect should be linear in the equivalent concentration, but in the acetates the salt effect should be "parabolic,"[2] that is to say, particularly pronounced at low concentrations. We shall see that these theoretical predictions are verified by our experiments.

III. EXPERIMENTAL PROCEDURE

Two different experimental procedures were made use of in the colorimetric measurement of the ratio $C_{I^{--}}/C_{HI^-}$. Our early measurements were made with test tubes, selected with bores uniform to within 4 per cent, in a comparator rack exactly as described by Clark (4). The difference between the values of the color ratios of two successive standards in the center range was approximately 12 per cent. The color of an unknown buffer–indicator solution could be interpolated between successive standards to quarters, and so the color ratio C_I/C_{HI} measured with an accuracy of only about ± 3 per cent.

Each color standard when prepared was freed from oxygen by bubbling nitrogen through the tube and the solution was corked in an atmosphere of nitrogen. In spite of this, it was found that the color of the basic solutions faded. The precaution was therefore taken of preparing new standards at least once a week. Kilpatrick and Chase (12) attribute this fading of the basic form of the indicator to a replacement of the bromine in the indicator compound by a hydroxyl group. They state that the greater the concentration of the hydroxyl ion, the faster the color of the indicator will fade.

Our later measurements were made with a colorimeter of the Gillespie

[2] In the limit of small concentrations the law

$$-\log_e f = AC^n$$

is of the same form as

$$1-f = AC^n$$

It is therefore natural to speak of a "linear" effect when n is unity. In the case that n is one half, we may speak of a "parabolic" effect because if f be plotted against C the curve will be a parabola. Many authors refer to such a law as an "exponential" effect, but this terminology is ambiguous. For f is an exponential function of C when n is unity ("linear" effect). When n is one half ("parabolic" effect), f is an exponential function of $C^{1/2}$.

type made by the Bausch and Lomb Optical Company, used as described by Clark (reference 4, p. 168). The total thickness of solution looked through was in all cases 20 mm., so that the ratio C_{I^-}/C_{HI^-} was equal to $20 - x/x$, where x was the reading of the colorimeter which could be determined to within 0.05 mm. The reproducibility of results was on the average within 1 per cent. The colorimeter was not only more accurate but also more convenient to use. As new bicolor standards were prepared each day, there was no risk of fading.

The stock indicator solutions were prepared according to the directions given by Clark (reference 4, p. 91) and were kept in the dark. In the actual solutions with which measurements were made the concentration of indicator was approximately 6×10^{-5} molar.

The bromothymol blue was obtained from Coleman and Bell Company. Four samples of bromocresol green were used. The first was obtained from the Eastman Kodak Company; the second by recrystallization of the first from glacial acetic acid. The third sample was obtained from Hynson, Westcott and Dunning, Inc.,[3] and the fourth by recrystallization of the third from glacial acetic acid.

The potassium chloride was Baker's "analyzed," which we recrystallized. The hydrochloric acid solutions were made from some constant boiling mixture, which, as well as some carbon dioxide-free sodium hydroxide, was kindly supplied by Mrs. Laing McBain. The acetic acid was standardized by titration against the sodium hydroxide, which in turn was standardized against the hydrochloric acid. The sodium acetate was prepared from the acetic acid and the sodium hydroxide. All the phosphate was obtained from a preparation of Merck described as anhydrous Na_2HPO_4. Electrometric titrations and determinations of loss of weight on ignition, however, convinced us that this preparation, while dry, contained between 1.5 and 1.6 moles per cent of NaH_2PO_4. All solutions were made from ordinary distilled water freed from carbon dioxide by bubbling nitrogen through it.

All measurements were made in daylight using a north light. Before making measurements, the indicator–buffer solutions were put in test tubes and brought to 25°C. in a thermostat.

IV. EXPERIMENTAL RESULTS AND ACCURACY

All measurements were made at 25°C. The experimental results are conveniently given in tabular form. Table 1 gives an example of the results obtained with the colorimeter using buffers of approximately 0.05 equivalent concentration. The first three columns give the concentration of the various anions in each solution, the cations being in all cases Na^+. The fourth column gives the ratio of the concentrations of primary phos-

[3] This sample was donated by Hynson, Westcott and Dunning, Inc., for which we wish to express our thanks.

phate to secondary phosphate; the fifth column gives the reading x of the colorimeter; the sixth column gives the observed ratio of basic to acid form of bromothymol blue indicator; and the seventh column gives K_C obtained as the product of the values in the fourth and sixth columns. It will be noticed that K_C is, within the experimental error, a constant at the given total equivalent concentration. In the test tube measurements it was found that at each total equivalent concentration K_C is constant to within ±4 per cent, whereas in the colorimeter measurements at each total equivalent concentration K_C was found constant to within ± 1.5 per cent. At each total equivalent concentration the colorimeter measurements confirmed the test tube measurements within the degree of accuracy of the latter.

TABLE 1

Colorimeter measurements with bromothymol blue

Total equivalent concentration = 0.0496

$C_{Cl} \times 10^2$	$C_{H_2PO_4^-} \times 10^2$	$C_{HPO_4^{--}} \times 10^2$	$\frac{C_{H_2PO_4^-}}{C_{HPO_4^{--}}}$	x	$\frac{C_{I^-}}{C_{HI}}$	$\frac{C_{I^-} \cdot C_{H_2PO_4^-}}{C_{HI} \cdot C_{HPO_4^{--}}}$
0 40	0 44	2 06	0 213	5 5	2 64	0 56
0 60	0 64	1 86	0 345	7 45	1 68	0 58
0.80	0 84	1 66	0 510	9 4	1 13	0 58
1 00	1 04	1 46	0 710	11 1	0 802	0.57
1 20	1 24	1 26	0 984	12 7	0 575	0 57
1 40	1 44	1 06	1 36	14 1	0 418	0 57
1 60	1 64	0 86	1 91	15 4	0 299	0 57
1 80	1 84	0 66	2 79	16 65	0 201	0 56
Average $K_C = \frac{C_{I^-} \cdot C_{H_2PO_4^-}}{C_{HI}\ C_{HPO_4^{--}}}$						0 57±0 007

There is no trend in the values of K_C from the basic to the acid forms of the buffer in table 1. But in more dilute solutions, there was a definite trend which became more pronounced with dilution. This trend in the value of K_C is illustrated by table 2 where the values of K_C range from 0.51 to 0.60. This is probably due to the solutions becoming accidentally contaminated with carbon dioxide, although every precaution was taken to remove carbon dioxide from the water used to make up the solutions. This effect was observed only at equivalent concentrations of 0.005 and below. It increased rapidly at lower concentrations. At these concentrations the values of K_C given by the more basic solutions were rejected. This seems justifiable because there was no corresponding trend observed in the values of K_C for the acetate buffer and bromocresol green, even in concentrations as low as 0.002.

TABLE 2

Colorimeter measurements with bromothymol blue

Total equivalent concentration = 0.00496

$C_{Cl^-} \times 10^2$	$C_{H_2PO_4^-} \times 10^2$	$C_{HPO_4^{--}} \times 10^2$	$\frac{C_{H_2PO_4^-}}{C_{HPO_4^{--}}}$	x	$\frac{C_{I^{--}}}{C_{HI^-}}$	$\frac{C_{I^{--}} - C_{H_2PO_4^-}}{C_{HI^-} - C_{HPO_4^{--}}}$
0.40	0.44	2.06	0.214	5 9	2.39	0.51
0.60	0.64	1 86	0.344	7 8	1.56	0 54
0.80	0.84	1 66	0.506	9 5	1.11	0.56
1.00	1.04	1.46	0 712	11.05	0.810	0.57
1.20	1.24	1.26	0.984	12.55	0.594	0.585
1.40	1.44	1 06	1.38	14 0	0.429	0.59
1.60	1.64	0.86	1 91	15.25	0.311	0.59
1.80	1.84	0 66	2 79	16 45	0 216	0 60
1.90	1 94	0 56	3 43	17.05	0.173	0 60

TABLE 3

Colorimeter measurements with bromocresol green

Total equivalent concentration = 0.10

$C_{Cl^-} \times 10$	$C_{HAc} \times 10$	$C_{Ac^-} \times 10$	$\frac{C_{HAc}}{C_{Ac^-}}$	x	$\frac{C_{I^-}}{C_{HI}}$	$\frac{C_{I^-} - C_{HAc}}{C_{HI^-} - C_{Ac^-}}$	INDICATOR SAMPLE*
0 24	0 24	0.76	0.316	5 7	2 51	0 79	a
0.32	0 32	0 68	0.471	7 3	1 74	0 82	a
0 40	0 40	0.60	0 666	8 95	1 23	0 82	a
0 40	0 40	0.60	0 666	8 95	1 23	0 82	b
0 40	0 40	0 60	0 666	9 0	1 22	0 81	c
0.40	0 40	0 60	0 666	8 95	1 23	0 82	d
0 48	0 48	0 52	0 923	10 6	0 877	0 81	a
0 56	0 56	0 44	1 27	12 1	0 653	0 83	a
0 56	0 56	0 44	1.27	12 15	0 646	0 82	b
0.56	0 56	0 44	1 27	12 1	0 653	0 83	c
0.56	0 56	0.44	1 27	12 15	0 646	0 82	d
0.64	0.64	0 36	1 78	13 7	0 460	0 82	a
0 72	0.72	0.28	2.57	15 15	0 320	0 82	a
0.80	0 80	0.20	4 00	16 6	0 205	0 82	a
0 80	0 80	0 20	4.00	16 6	0 205	0 82	b
0 80	0 80	0 20	4 00	16.6	0 205	0 82	c
0 80	0 80	0 20	4 00	16 6	0 205	0.82	d
0 88	0 88	0 12	7 33	18 0	0 111	0 81	a
Average $K_C = \frac{C_{I^{--}} - C_{HAc}}{C_{HI} \quad C_{Ac^-}}$						0 82±0.008	

* Bromocresol green indicator samples: (a) obtained from Eastman Kodak Company; (b) same as a, but recrystallized from acetic acid; (c) donated by Hynson, Westcott, and Dunning, Inc., (d) same as c, but recrystallized from acetic acid.

Table 3 gives results obtained with the colorimeter using the acetate buffer with bromocresol green. All columns have the same interpretation as in table 1, except that there is an extra column giving the sample of indicator used in each measurement which is explained in the footnote. It is clear that the values of K_C obtained for the four samples are identically equal. All the measurements made with the acetic acid-acetate buffer and bromocresol green were measured with the colorimeter. No trend in the values of K_C was observed even at concentrations as low as 0.002.

All the results for measurements at various concentrations are collected in tables 4 and 5. Table 4 gives the results for both test tube and color-

TABLE 4

K_C values for bromothymol blue phosphate buffer equilibrium

TOTAL EQUIVALENT CONCENTRATION	$K_C = \frac{C_{I^-}\ C_{H_2PO_4^-}}{C_{H^-}\ C_{HPO_4}}$	ROOT MEAN SQUARE DEVIATION	METHODS* USED TO MEASURE $\frac{C_{I^-}}{C_{HI^-}}$
0 00245	(0 60)	—	a
0 00496	(0 595)	—	a
0 00496	(0 58)	—	b
0 00995	0 59	±0 007	a
0 00993	0 59	±0 01	b
0 01983	0 58	±0 02	b
0 04963	0 57	±0 007	a
0 04963	0 57	±0 02	b
0 09925	0.54	±0 005	a
0 09925	0.56	±0 02	b
0 19850	0 48	±0 008	a

* Methods used to measure ratio $\frac{C_{I^-}}{C_{HI^-}}$: (a) colorimeter; (b) bicolor standards in test tubes.

The values of K_C for the most dilute solutions given in parentheses were obtained from the more acid solutions, the more basic ones being rejected.

imeter measurements for bromothymol blue and phosphate buffer. It is seen that these two sets of measurements agree within the experimental error of the test tube set. Table 5 gives the results for all four samples of bromocresol green and acetate buffer.

V. THEORETICAL DISCUSSION

The values of K_C given in tables 4 and 5 are plotted against total salt concentration in figures 1 and 2. First, considering bromothymol blue in the primary–secondary phosphate buffer, we see in figure 1 that the "salt effect" is linear in the concentration. This is in accordance with the theory, because both indicator and buffer are of the same electric type.

TABLE 5

K_C values for bromocresol green acetate buffer equilibrium

TOTAL CONCENTRATION	$C^{1/2}$	$K_C = \frac{C_{I^{--}} C_{HAc}}{C_{HI^-} C_{Ac^-}}$	ROOT MEAN SQUARE DEVIATION	DETERMINATIONS*
0.002	0.045	0.65	±0.015	a
0.002	0.045	0.65	±0.01	b
0.005	0.071	0 67	±0.01	a
0.005	0.071	0.67	±0.01	b
0.010	0.100	0.69	±0 009	a
0.010	0.100	0.70	±0 007	b
0.020	0.142	0.72	±0.01	a
0.020	0.142	0 73	±0 007	b
0.050	0 224	0 77	±0 008	a
0.050	0.224	0 78	±0 007	b
0 100	0 316	0 82	±0 01	b
0.200	0 446	0 86	±0 005	b

* The measurements marked a were made at an earlier stage of our investigation than those marked b.

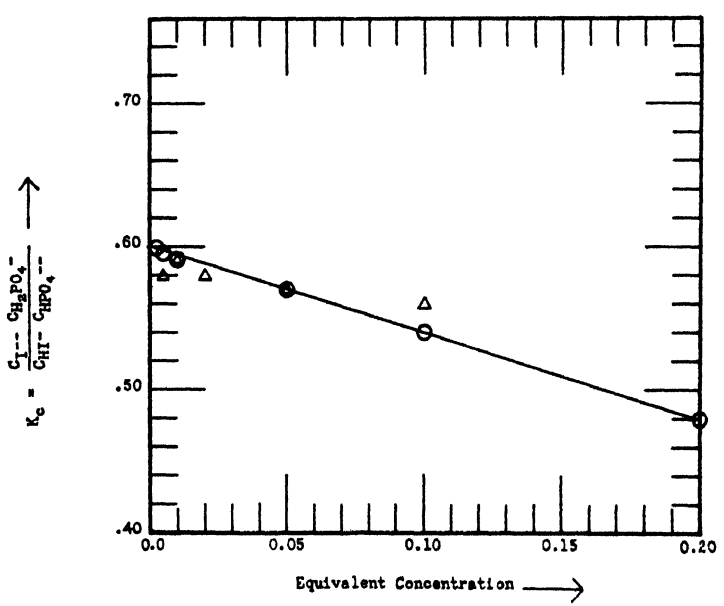


FIG. 1

△ Test tube measurements
○ Colorimeter measurements

Assuming that the trend in dilute solutions is due to contamination by carbon dioxide and that the more acid solutions give the correct values of K_C, the extrapolation is small and fairly safe. The extrapolation gives 0.60 as the value for the ratio $K_{HI}/K_{H_2PO_4^-}$ where K_{HI^-} and $K_{H_2PO_4^-}$ are the true thermodynamic acid constants of bromothymol blue and of $H_2PO_4^-$ respectively.

On the other hand, if we observe the shape of the curve for bromocresol green in the acetic acid-acetate buffer in figure 2, we find a pronounced curvature even at low concentrations, which makes extrapolation more uncertain. This pronounced "salt effect" at low concentrations is in accord-

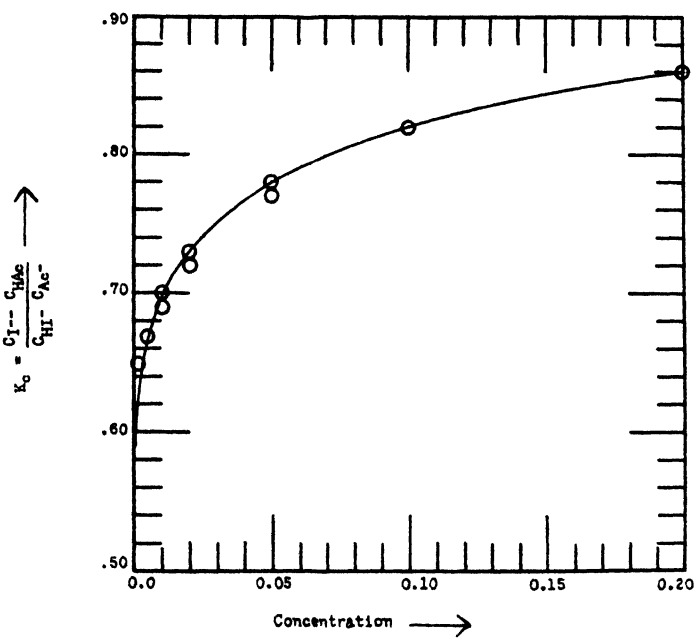


FIG. 2

ance with the theory due to the fact that the indicator and buffer are of different electric types. Formula 17 leads to a limiting law at infinite dilution

$$-\log_{10}\frac{f_{HI^-} \cdot f_{Ac^-}}{f_{I^{--}} \cdot f_{HAc}} = -1.0\, C^{1/2} \tag{18}$$

or

$$\frac{f_{HI^-} \cdot f_{Ac^-}}{f_{I^{--}} \cdot f_{HAc}} = 1 + 2.30\, C^{1/2} \tag{19}$$

If then we plot K_C against $C^{\frac{1}{2}}$ and extrapolate, the curve should have at zero concentration a finite slope equal to the product of 2.30 and the limit-

ing value of K_C. This is shown in figure 3. If this extrapolation is correct, the value of K_{HI}/K_{HAc} is 0.59, where K_{HI} and K_{HAc} are the true thermodynamic acid constants of bromocresol green and acetic acid respectively.

In figure 3 are included values of $C_{I^{--}} \cdot C_{HAc}/C_{HI^{-}} \cdot C_{Ac^{-}}$ for bromocresol green calculated from the test-tube experiments of Sendroy and Hastings (15), all of which were made with only one buffer ratio $C_{HAc}/C_{Ac^{-}}$ equal to 0.233. We have no explanation of the large discrepancy between their

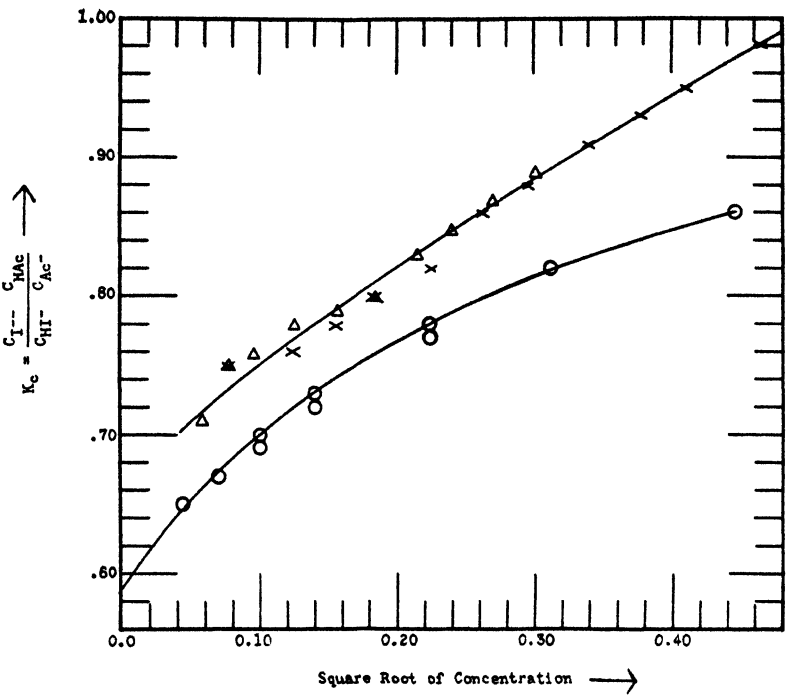


FIG. 3

○ Our measurements
Hastings and Sendroy's measurements:
△ In HAc + NaAc
× In HAc + NaAc + NaCl

results and ours, especially as they also used bromocresol green obtained from Hynson, Westcott and Dunning.

VI. ACID CONSTANT OF BROMOCRESOLGREEN

Having obtained values of K_C or $K_{(C)HI}/K_{(C)HA}$ experimentally and values of K_{HI}/K_{HA} by extrapolation, if we have independent values of $K_{(C)HA}$ or K_{HA}, we can by multiplication calculate values of $K_{(C)HI}$ or K_{HI} for the indicator.

In the case of acetic acid reliable data are available for K_{HA}. Harned

and Ehlers (11) have evaluated K_{HAc} by electrometric measurements without liquid junction potentials. Combining their value 1.75×10^{-5} for K_{HAc} with our value 0.59 for K_{HI}/K_{HAc}, we obtain 1.03×10^{-5} as the value for the true thermodynamic acid constant K_{HI} of bromocresol green. This is probably accurate to within 1 or 2 per cent.

The $K_{(C)HI}$ value of bromocresol green in an acetate buffer solution at a salt concentration of 0.10 molar may be estimated as follows. According to the very accurate measurements of Güntelberg (9) the value of f_{HCl} in 0.1 M sodium chloride is 0.79. If we assume this same value for $f_{H,Ac}$, the mean activity coefficient of the hydrogen and acetate ions in an acetate buffer of total salt concentration 0.1, the error can hardly be more than 2 or 3 per cent. On this assumption we obtain for $K_{(C)HI}$ at an ionic strength 0.1 the value 2.30×10^{-5} with a probable accuracy of about 5 per cent.

The perfect agreement between this value and that of 2.33×10^{-5} computed by Kilpatrick and Chase (12) from the data given by Kolthoff is fortuitous, as the accuracy claimed for Kolthoff's value is only 12 per cent. Kilpatrick and Chase have themselves made a study of the "salt effect" of bromocresol green in buffers of benzoic acid–benzoate, acetic acid–acetate, and hexahydrobenzoic acid–hexahydrobenzoate. Their measurements were mostly at concentrations greater than those used by us, their lowest salt concentration being 0.1 molar. At this concentration they assign the value 3.07×10^{-5} to $K_{(C)HI}$ of bromocresol green. We are unable to explain the discrepancy between this value and ours. It is only partially accounted for by the dependence of Kilpatrick and Chase's values on electrometric measurements of cells with liquid–liquid junctions. For, according to a private communication from Dr. Kilpatrick, their mean values for the ratio $C_{I^{--}}\ C_{HAc}/C_{HI^{-}}\ C_{Ac^{-}}$ in 0.1 M acetate buffers were 0.94 with a commercial sample of indicator and 1.03 with a special sample of indicator, as compared with our value 0.82. The discrepancy can hardly be due to difference in the indicator sample, as we obtained identical values with all four samples and that obtained from Hynson, Westcott and Dunning was the same preparation as supplied by them to Kilpatrick and Chase.

VII. ACID CONSTANT OF BROMOTHYMOL BLUE

To determine the acid constant of bromothymol blue from our value of $K_{HI}/K_{H_2PO_4^-}$ we require to have a value for $K_{H_2PO_4^-}$. No values are available for this quantity other then those obtained by means of cells with liquid–liquid junctions. Bjerrum and Unmack (1) on the basis of such measurements assign the value 6.20×10^{-8} to $K_{H_2PO_4^-}$ at 25°C. According to electrometric measurements described in another paper (8) we are able to confirm Bjerrum and Unmack's experimental electromotive force values to within 0.4 millivolt, but for reasons there given we consider that a more probable value for $K_{H_2PO_4^-}$ is 5.97×10^{-8}. Combining this

value of $K_{H_2PO_4^-}$ with an extrapolated value 0.60 for $K_{HI}/K_{H_2PO_4^-}$, we obtain for the thermodynamic acid constant K_{HI} of bromothymol blue the value 3.58×10^{-8} with an estimated accuracy of 2 or 3 per cent.

For the reasons given above we prefer to give our results mostly in a form independent of computations based on electrometric measurements of cells with liquid–liquid junctions. We have, however, for the sake of comparison with values given by Kolthoff (13), combined our colorimetric data with our electrometric data to compute values of $-\log_{10}C_{H^+}f_{H^+}\cdot C_I/C_{HI}$

TABLE 6

Ionic strength	0 0125	0.10	0.125	0.15	0.25
Our pK_1 values	7.30		7.10		7.05
Kolthoff's pK_1 values		7.10		7.06	

called pK_1 by Kolthoff. As seen from table 6 our values are in good agreement with those given by Kolthoff.

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NEW BOOKS

The Sanitation of Public Water Supplies. By MURRAY P. HORWOOD. 15 x 23 cm.; 181 pp. Baltimore: Charles C. Thomas, 1932.

In the first chapter, dealing with public health activity, the author divides the history of development of the field into successive periods in which the sanitary engineer, the bacteriologist, and the physiologist exercised a dominant influence. He regards the control of environment as principally responsible for advances made —an opinion which will not be shared by many public health workers. A more extended discussion of vital statistics would be a welcome addition to this chapter. In chapters II and III the development of public water supplies is treated historically and statistically; information concerning several large cities is cited. Chapter IV discusses the requirements of drinking water, dealing with physical, mineral, and bacteriological standards. The relation of water and disease is comprehensively treated in chapter V, particular attention being given to typhoid fever.

Methods of water treatment are detailed in chapters VI to X, inclusive, titled successively: "The Purification and Improvement of Water Supplies," "Water Softening," "Slow Sand Filtration," "Rapid Sand Filtration," and "Disinfection." The chapters on "Softening" and "Rapid Sand Filtration" are exceptionally good, typical chemical reactions and descriptions of operating conditions characterizing the discussion. Disinfection by use of hypochlorite, chlorine, and chloramine, with discussion of the chemical "mechanism" is treated in the final chapter, with methods of use for various conditions. The use of ultra-violet light is also described.

The material in this book covers the title comprehensively in an elementary manner, and it should be of value to the general reader, although each technical reader perhaps would prefer to arrange and emphasize the material differently while agreeing that its selection is substantially satisfactory.

FREDERIC BASS.

Phase Rule Studies. By J. E. WYNFIELD RHODES. 19 x 13 cm.; x + 131 pp. London: Oxford University Press, 1933. Price: $2.25.

In the introduction E. L. Rhead says: "Owing to its many practical applications a knowledge of the Phase Rule has become indispensable in the equipment of the modern chemist. . . . The Phase Rule is capable of application in many directions, not only to subjects that are palpably chemical in their nature, but to others that are not essentially so, or, at any rate, are not usually approached from a chemical standpoint. The principles of the Phase Rule are eminently applicable in geology, mineralogy, and metallurgy, although the introduction is generally by avenues other than a course in pure Chemistry."

The chapters are entitled: introductory; one-component systems; two-component systems in which mixed crystals are not formed; two-component systems in which mixed crystals are formed; three-component systems, isothermal diagrams; three-component systems, the polythermal model and its projections; miscellaneous applications of the phase rule; systems of four or more components and their graphical representation; experimental methods employed in phase rule work.

Short as this book is, the author suggests that "students who do not need the whole of the subject matter of this book but desire only to make a general survey, should read chapters I, II, III, IV, and IX."

WILDER D. BANCROFT.

The Lyophilic Colloids (Their Theory and Practice). By MARTIN H. FISHER and MARIAN O. HOOKER. 240 pp.; 84 illustrations; 3 parts. Springfield, Illinois, and Baltimore, Maryland: Charles C. Thomas, 1932. Price $4.25.

This book contains the work of the authors during the last fifteen years. The first two-thirds is devoted to a general discussion of lyophilic colloids. In this first part the authors develop the idea from such systems as phenol-water, quinoline-water, and gelatin-water, of the solution of water in these various substances, as well as the solution of these substances in water. This is the central theme of the book. Extensive usage is made of resistance measurements. The authors plunge themselves into a wilderness of heterogeneous systems without adequate physicochemical tools. The result is confusion. It seems meaningless to the reviewer to distinguish in kind between a solution of phenol in water and that of water in phenol. H. R. Kruyt and H. G. B. de Jong receive no recognition.

The second part is devoted to chemical applications. Here again they emphasize the idea of mutual solubility. They state that when dealing with lyophilic systems ". . the electrical properties, ions, isoelectric points, Donnan equilibria and pHs and CHs all pass out of the picture." There are short sections on greases and the livering of points.

The third section deals with the biological applications. They criticize the osmotic concept of the cell and point out the prevailing confusion in these matters. They discuss a colloid chemical theory of water absorption based on their concepts. They adduce for proof that protoplasm is a solution of water in X, the fact that a man may go in swimming or be rained upon and not dissolve. They declare that there is no free water in protoplasm but they fail to note that there has been an increasing effort on the part of chemists and physiologists to devise accurate methods to determine the exact state of this water and thus dispense with vague speculations.

This book makes interesting reading. It gives us a description of the bogs and morasses from which colloid chemistry emerged some fifteen years ago.

HENRY B. BULL.

Struktur der Materie: vier Vorträge. By P. DEBYE. 22 x 15 cm.; iv + 50 pp. Leipzig: S. Hirzel, 1933. Price (stiff paper covers): 3 R. M.

The subjects of the four lectures are: (1) Interferometric measurement of molecular structures; (2) Electrical structure of molecules; (3) Molecular structure of liquids; (4) Structure of electrolytic solutions. The book deals exclusively with modern developments—such as the application of x-ray and electron diffraction to stereochemical problems, the determination of dipole moments, and other typical branches of the beautiful work with which Debye and his school have been so closely associated during the past decade.

The treatment is entirely elementary and descriptive. The booklet provides an excellent and stimulating survey for non-specialists and young students; its value would be appreciably enhanced by the addition of even a few references to original papers.

H. R. ROBINSON.

THE DECOMPOSITION OF α-NITROCARBOXYLIC ACIDS

WITH SOME REMARKS ON THE DECOMPOSITION OF β-KETOCARBOXYLIC ACIDS

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The object of this paper is to contribute to our understanding of the tendency of α-nitrocarboxylic acids to split off carbon dioxide.

$$> CNO_2 \cdot COOH \longrightarrow > CHNO_2 + CO_2$$

The simplest acid of this type, nitroacetic acid, was studied kinetically by Heuberger (2, 3) and, independently, by the author of this paper (7). In the latter work, the rate of decomposition was determined on solutions of hydrochloric acid of various concentrations and in buffer solutions, mainly acetate buffers (pH = 4 to 5). The rate increases with decreasing hydrogen-ion concentration and reaches a maximum value in the acetate buffers. Here it is independent of the hydrogen-ion concentration. In sufficiently alkaline solution nitroacetic acid is stable.

While the free nitroacetic acid consists of two tautomers

$$O_2N \cdot CH_2 \cdot COOH \quad \text{and} \quad HOON{:}CH \cdot COOH$$

there are three possible forms of the univalent nitroacetate ion

$$O_2N \cdot CH_2 \cdot CO_2^-, \quad {}^-O_2N{:}CH \cdot COOH, \quad \text{and} \quad HOON{:}CH \cdot CO_2^-$$

and only one divalent ion

$${}^-O_2N{:}CH \cdot CO_2^-$$

The experiments agree with the assumption that both the free acid and the divalent ion are stable, while one of the univalent ions is unstable. From the experiments the first dissociation constant of nitroacetic acid (about 0.02) was calculated. It could not be settled from the experiments on nitroacetic acid which of the three forms of the nitroacetate ion is unstable, or, in other words, whether the instability of the α-nitrocarboxylic acids is connected with the formation of an aci-form of the nitro compound. In order to solve this problem α-nitroisobutyric acid (dimethyl-

nitroacetic acid) is studied in the present paper. This substance is not a pseudo acid. It forms only the ion $O_2NC(CH_3)_2CO_2^-$. It is found that it splits off carbon dioxide in the same way as nitroacetic acid and with a similar velocity. Consequently, the unstable form of the α-nitrocarboxylic acids is the ion $>CNO_2 \cdot CO_2^-$.

However, while nitroacetic acid gives carbon dioxide and nitromethane as final reaction products, the carbon dioxide cleavage of α-nitroisobutyric acid in hydrochloric acid is followed by a secondary reaction by which more gas is developed. From the experimental results given below the following mechanism is suggested

$$O_2NC(CH_3)_2CO_2^- \rightarrow {}^-O_2N{:}C(CH_3)_2 + CO_2 \quad (1)$$
$$H^+ + {}^-O_2N{:}C(CH_3)_2 \rightarrow HOON{:}C(CH_3)_2 \quad (2)$$
$$HOON{:}C(CH_3)_2 \rightarrow OC(CH_3)_2 + \tfrac{1}{2}N_2O + \tfrac{1}{2}H_2O \quad (3)$$

Reaction 1 is followed by the instantaneous reaction 2, and this by the decomposition 3. In not too weak hydrochloric acid, reaction 3 is so much quicker than reaction 1 that the carbon dioxide cleavage determines the velocity of the total reaction.

In acetate buffer solutions the production of gas in excess of one mole per mole of α-nitroisobutyric acid is extremely slow. Probably the aci-form produced by reaction 2 is transformed into the nitro compound

$$HOON{:}C(CH_3)_2 \rightarrow O_2NCH(CH_3)_2 \quad (4)$$

sufficiently quickly to avoid the decomposition 3. This quick rearrangement in the acetate buffer is in conformity with earlier work (10) in which it was found that the prototropic isomerization of aliphatic nitro compounds is catalyzed by acetate ions and other bases.

α-Nitroisobutyric acid was prepared by the method of Steinkopf and Supan (14). The beautiful white crystals obtained were used for the kinetic experiments without purification. The acid could only be recrystallized with very great loss. When an experiment was repeated with different preparations (m.p., 93–95°C.) concordant results were obtained.

The decomposition was investigated at 17.84 and at 9.78°C. Experiments were carried out in hydrochloric acid and acetate buffer solution by observing the increase in pressure above the solution during reaction by means of an apparatus described in an earlier paper (9).

For comparison some experiments on nitroacetic acid were carried out under the same circumstances. The substance was prepared as described in the paper on nitroacetic acid (7).

When a little nitroisobutyric acid was dissolved in barium hydroxide the solution kept clear for some seconds. Then a precipitate of barium carbonate began to be formed. This shows that the nitroisobutyrate ion is unstable.

EXPERIMENTS IN ACETATE BUFFER SOLUTIONS

Here

c = the initial concentration of the reacting acid.

$c - x$ = its concentration t minutes after the start.

P = the difference between the final pressure readings and the reading at the time t.

P_0 = the value of P, when $t = 0$.

ϕ = the proportionality factor $P_0/c = P/(c - x)$ (cm. of mercury per mole per liter).

k^* = unimolecular velocity constant. By an asterisk we denote that the constant has been calculated by means of decadic logarithms. k^* is computed in the usual way by plotting log P against t.

The agreement with the unimolecular law is good. The carbon dioxide cleavage was finished a few hours after the start. After that time a very slow pressure increase was noticed. This secondary reaction was sufficiently slow to allow an accurate determination of the end point of the primary reaction. When the primary reaction was near its end the solution assumed a greenish color.

The results of experiments in different acetate buffer solutions are given in table 1. Each experiment was carried out with 60 cc. of solution and enough nitroisobutyric acid to make it 8 to 10 $\times$ $10^{-3}M$. The total pressure increase (about 6 cm. of mercury) corresponds to an average value of $\varphi = P_0/c = 643$ for the experiments at 17.84°C. This is only 3.4 per cent more than the value $\varphi = 622$ found by adding a known amount of sodium carbonate to 60 cc. of the acetate buffer. The discrepancy may be due to a small vapor pressure of the other reaction product. Hence, one mole of carbon dioxide is produced per mole of nitroisobutyric acid in the acetate buffers.

As seen from table 1 the velocity of decomposition is not affected by a considerable variation of the ratio between the concentrations of acetic acid and sodium acetate. In the last experiment at 17.84°C. the final pressure was not determined as accurately as usual. It was therefore omitted when taking the mean values. The fourth column gives the number of the preparation of nitroisobutyric acid. It is seen that different preparations decompose with the same velocity.

In table 2 are given the results of experiments on the decomposition of nitroacetic acid carried out under the same experimental conditions.

EXPERIMENTS IN HYDROCHLORIC ACID

Here the pressure increase was approximately one and a half times as great as would be expected from the experiments in acetate buffer solutions. According to the mechanism suggested in the schemes 1 to 3, one

mole of carbon dioxide and half a mole of nitrous oxide should be produced per mole of nitroisobutyric acid. In order to test this assumption the following calculations were carried out.

First the total volume, v cc., of the reaction vessel was determined by adding a known amount of sodium carbonate to the flask which contained a known volume, u cc., of 0.1 M hydrochloric acid at 17.84°C. If we denote by p_0 (cm. of mercury) the pressure increase per mole of sodium carbonate and by f the Ostwald absorption coefficient (the ratio between the concentrations of a gas in liquid and gaseous phase at equilibrium), the following formula holds

$$p_0 (v - u + fu) = RT$$

where $RT = 1.815 \times 10^6$. From the investigation of Geffcken (1) we find for carbon dioxide at 17.84°C. $f = 0.988$. The results are given in table 3. The average value of the volume is $v = 173.6$ cc.

TABLE 1

Decomposition of α-nitroisobutyric acid in acetate buffer solutions

TEMPERATURE	(CH_3COOH)	(CH_3CO_2Na)	PREPARATION	φ	k^*
degrees C.					
17.84	0.100	0.100	1	646	0.0449
	0.100	0.100	1	641	0.0446
	0 050	0.050†	1	643	0.0449
	0.050	0 100	1	642	0.0448
	0.180	0.100	1	(652)	(0 0440)
Average values				643	0.0448
9.78	0.100	0 100	1	570	0.01396
	0.100	0.100	3	575	0.01394
Average values				572	0 01395

† Containing 0.050 M sodium chloride

TABLE 2

Decomposition of nitroacetic acid in acetate buffer solutions

TEMPERATURE	(CH_3COOH)	(CH_3CO_2Na)	k^*	AVERAGE VALUE OF k^*
degrees C.				
17.84	0 100	0.100	0.02464	0.02460
	0.100	0.100	0.02456	
	0.050	0 050	0.02460	
9.78	0.100	0.100	0.00772	0.00774
	0.100	0.100	0.00776	

The molar pressure increase p_2 for nitroisobutyric acid added to hydrochloric acid is given in the fifth line of table 3. By subtraction of p_0, the molar pressure increase for sodium carbonate added to hydrochloric acid, we find the partial pressure p_3 (per mole of nitroisobutyric acid) of the gas which is produced in addition to the carbon dioxide. If we assume that n moles of a gas with the absorption coefficient f is produced per mole of the acid, we have

$$p_3(v - u + fu) = nRT$$

or

$$173.6p_3 = 1.815 \times 10^6\, n + (1 - f)\, p_3u$$

When the experimental values of u and p_3 are introduced we get as result $n = 0.538$ mole of a gas with the absorption coefficient $f = 0.728$ (compare

TABLE 3

u, volume of solution	20	60	100
p_0, pressure increase per mole of Na_2CO_3 in 0.1 M HCl	1.042×10^4	1.046×10^4	$1\ 061\times10^4$
v, total volume of vessel	174 3	174 2	172.2
p_1, pressure increase per mole of nitroisobutyric acid in acetate buffers	($1\ 068\times10^4$)	$1\ 072\times10^4$*	($1\ 088\times10^4$)
p_2, pressure increase per mole of nitroisobutyric acid in 0.03–0.3 M HCl	$1\ 623\times10^4$	1.667×10^4†	1.729×10^4
$p_3 = p_2 - p_0$ (observed)	$0\ 581\times10^4$	$0\ 621\times10^4$	$0\ 668\times10^4$
p_3 (calculated from $f = 0.728$ and $n = 0.538$)	$0\ 581\times10^4$	$0\ 621\times10^4$	$0\ 667\times10^4$
$p_4 = p_2 - p_1$ (observed)	$0\ 555\times10^4$	$0\ 595\times10^4$	0.641×10^4
p_4 (calculated from $f = 0.716$ and $n = 0.513$)	0.554×10^4	$0\ 594\times10^4$	$0\ 641\times10^4$

* Average of four experiments (table 1).
† Average of six experiments (table 4).

the sixth and seventh line of table 3). From Geffcken's paper we get for nitrous oxide at 17.84°C. $f = 0.718$.

If instead of subtracting the molar pressure increase for sodium carbonate in hydrochloric acid we subtract that for nitroisobutyric acid in acetate buffers (p_1), we get an even better agreement. Only the value of p_1 for 60 cc. of buffer solution has been determined by experiment. For the calculation of the values in parentheses we have used the assumption that the ratio p_1/p_0 is independent of the volume u. We find (compare the last two lines of the table) $n = 0.513$ and $f = 0.716$.

In order to show that one mole of acetone is formed per mole of nitro-

isobutyric acid (scheme 3), samples were taken from the reaction vessel after some of the experiments. Acetone was determined by the method of Messinger (6) in the form suggested by Ljunggren (5). By addition of sodium hydroxide and an excess of iodine solution iodoform was precipitated. The excess of iodine was titrated with thiosulfate after the solution had been acidified with sulfuric acid. The analysis gave as result that 0.96 to 1.00 moles of acetone had been formed per mole of nitroisobutyric acid. After the iodine set free by the addition of the acid had been titrated, more iodine was slowly liberated. The solution seemed to contain a substance which catalyzes the oxidation of hydriodic acid by the air. The deviation from 1.00 found in the analysis may have its origin in this source of error.

Shortly after the start of the reaction the solution assumed a light green color which vanished when the reaction was finished.

We shall now see that a comparison of the experiments in hydrochloric acid and acetate buffers leads to the following explanation. In the acetate buffers the acid is completely ionized and the velocity constant k found here is that for the decomposition of the nitroisobutyrate ion. In hydrochloric acid the fraction α which is ionized decomposes with the velocity constant k, while the unionized acid is stable. This is formally equivalent to saying that all the nitroisobutyric acid (free and ionized) decomposes with the velocity constant αk. We test the explanation by calculating the dissociation constant K of the nitroisobutyric acid from the degree of dissociation α found as the ratio between the velocity constants in hydrochloric acid and in acetate buffers.

We first assume that reaction 3 is so rapid compared with reaction 1 that the latter determines the velocity of the total reaction.

In computing the velocity constant we must take into account that the hydrogen-ion concentration of the solution of the acid in hydrochloric acid is diminished a little when the acid decomposes. We denote by a the concentration of hydrochloric acid, by α_0, α, and α_∞ the degrees of dissociation of the nitroisobutyric acid at the times 0, t, and ∞. According to the mass action law we have

$$\frac{\alpha}{1-\alpha}\,[a + \alpha\,(c - x)] = K$$

From this we obtain

$$\alpha = \frac{K}{a + \alpha(c - x) + K} \qquad \text{and} \qquad \alpha_\infty = \frac{K}{a + K} \tag{5}$$

The velocity is given by

$$\frac{dx}{dt} = k\alpha(c - x) \tag{6}$$

When equation 5 is introduced equation 6 may be written

$$k\alpha_\infty \mathrm{d}t = \left(\frac{1}{c-x} + \frac{\alpha_\infty}{a+K} - \frac{\alpha_\infty - \alpha}{a+K}\right)\mathrm{d}x$$

By integration we get

$$-k\alpha_\infty t = \text{const.} + l(c-x) + \frac{\alpha_\infty}{a+K}(c-x) - \int_c^{c-x} \frac{\alpha_\infty - \alpha}{a+K}\,\mathrm{d}(c-x)$$

If we introduce $P = \varphi\,(c - x)$, equation 5, and $k^* = 0.4343k$, we may write the expression as follows

$$-k^*\alpha_\infty t = \text{const.} + \log P + \beta P + \Delta \tag{7}$$

where

$$\beta \equiv \frac{0.4343K}{\varphi(a+K^2)}$$

and

$$\Delta \equiv \beta \int_{P_0-P=0}^{P_0-P} \frac{\alpha_\infty - \alpha}{\alpha_\infty}\,\mathrm{d}\,(P_0 - P) < \beta P_0 \frac{\alpha_\infty - \alpha_0}{\alpha_\infty}$$

For the calculation of the correction βP we must know K. This is found sufficiently accurately by calculating α_∞ from a preliminary value of the velocity constant $\alpha_\infty k$. The correction Δ is of no importance except in the most dilute solutions of hydrochloric acid. Here we may compute it by rough graphical integration.

The results of the experiments on nitroisobutyric acid are given in tables 4 and 5. The velocity constant $k^*\alpha_\infty$ is found by plotting the sum of log P and βP and, if necessary, the correction Δ against t. For the most concentrated solutions of hydrochloric acid we get points that fall well on a straight line. For 0.1 M and less concentrated acid the points fall on a curve which approaches more quickly to a straight line the more concentrated the acid. This result is what one would expect when a part of the gas is developed by a consecutive reaction whose velocity is less predominating the smaller the hydrogen-ion concentration. For the velocity constant $\alpha_\infty k^*$ of the primary reaction we take the numerical value of the slope of the straight line. While the approach to the straight line was sufficiently quick in 0.1 M hydrochloric acid to allow a good determination of $\alpha_\infty k^*$, this was uncertain even in 0.05 and 0.033 M, and in 0.02 and 0.01 M hydrochloric acid the straight line could not be drawn accurately enough. However, if we calculate $\alpha_\infty k^*$ for the experiment in 0.02 M HCl + 0.08 M NaCl according to the interpretation given above, using the dissociation constant K found for the same salt concentration in more acid solution, a line with the slope $-\alpha_\infty k^*$ fits well as an asymptote to the curve.

For the calculation of α_∞ from $\alpha_\infty k^*$ we use the value of k^* found in the experiments in acetate buffer solutions. It is seen from the tables that $K = a\frac{\alpha_\infty}{1 - \alpha_\infty}$ is constant when the concentration of hydrochloric acid is varied, while the total salt concentration is kept constant. In order to see if the values of K at different salt concentrations agree among them-

TABLE 4

Decomposition of α-nitroisobutyric acid in hydrochloric acid at 17.84°C.

(HCl)	PREPARATION	φ	$\alpha_\infty k^*$	α_∞	K	$-\log K$	μ	$-\log K + 0.998\sqrt{\mu}$	$1.928 + 0.873\mu$	$\delta \times 10^3$
0.3006	1	1006	0 003165	0.0706	0 0229	1.641	0 3008	2.190	2.190	0
0 1994	1		0.00445	0 0993	0.0220	1.657	0.1997	2.103	2.102	+1
0 1001	1	999	0 00746	0 1665	0 0200	1.699	0 1006	2 016	2.016	0
0 5005†	1	1000	0.01286	0.2870	0.0202	1.696	0.1009	2.013	2.016	−3
0 05005†	2	1000	0 01272	0 2839	0 0198	1.702	0 1009	2.019	2 016	+3
0.05005	1	997	0.01196	0.2670	0 0182	1 739	0 0509	1 964	1.972	−8
0 03337	1	997	0 01560	0 3482	0 0178	1.749	0 0345	1 935	1 958	−23
0.02016‡	1	(910)								
0.01008§	1	(991)								

† Containing 0.0500 *M* sodium chloride.
‡ Containing 0.0800 *M* sodium chloride.
§ Containing 0.0900 *M* sodium chloride.

TABLE 5

Decomposition of α-nitroisobutyric acid in hydrochloric acid at 9.78°C.

(HCl)	PREPARATION	$\alpha_\infty k^*$	α_∞	K	$-\log K$	μ	$-\log K + 0.986\sqrt{\mu}$	$1.871 + 0.873\mu$	$\delta \times 10^3$
0 3006	2	0 001052	0 0754	0 0245	1.611	0 3009	2 152	2.133	+19
0.2007	2	0.001548	0.1110	0.0251	1 601	0.2011	2 044	2.046	−2
0 2014	2	0 001538	0.1103	0 0250	1.603	0.2018	2 047	2 047	0
0 1004†	4	0.00276	0 1978	0 0248	1.606	0 2011	2 049	2 046	+3
0.1001	3	0 00257	0 1842	0 0226	1.646	0 1007	1.959	1.959	0
0 05005	3	0 00412	0 2953	0.0210	1.678	0 0512	1.902	1.916	−14

† Containing 0.100 *M* sodium chloride.

selves and to find the activity dissociation constant K_0 we proceed in the following way. According to the Debye-Hückel law we have

$$-\log K = -\log K_0 - A\sqrt{\mu} + B\mu \tag{8}$$

where μ is the ionic strength and A a constant (at 18°C. 0.998, and at 10°C. 0.986), while B approaches to a constant value when $\mu \to 0$. For μ we use a mean value found by adding $\frac{1}{2}\alpha_0 c$ to the sum of the concentrations of hydrochloric acid and sodium chloride. If we plot $-\log K + A\sqrt{\mu}$

against μ for each of the two series of experiments, the points fall fairly well on straight lines. Only the points for the most dilute hydrochloric acid deviate a little, probably owing to the greater error in computing the velocity constants. The neglect of these points in extrapolating to zero salt concentration is to some extent justified by the results on nitroacetic acid in hydrochloric acid (tables 6 and 7), where we have no con-

TABLE 6

Decomposition of nitroacetic acid in hydrochloric acid at 17.84°C

(HCl)	$\alpha_\infty k^*$	α_∞	K	$-\log K$	μ	$-\log K + 0.998\sqrt{\mu}$	$1.682 + 0.927\mu$	$\delta \times 10^3$
0.3006	0.002816	0.1145	0.0389	1.410	0.3011	1.959	1.960	−1
0.2007	0.00388	0.1577	0.0376	1.425	0.2015	1.874	1.869	+5
0.1000	0.00632	0.2569	0.0346	1.461	0.1014	1.779	1.775	+4
0.05010	0.00952	0.3870	0.0316	1.501	0.0519	1.728	1.730	−2
0.05010	0.00950	0.3862	0.0315	1.502	0.0519	1.729	1.730	−1
0.02014	0.01432	0.5821	0.0280	1.552	0.0228	1.703	1.703	0
0.01009	0.01777	0.7224	0.0262	1.581	0.0131	1.695	1.694	+1

TABLE 7

Decomposition of nitroacetic acid in hydrochloric acid at 9.78°C.

(HCl)	$\alpha_\infty k^*$	α_∞	K	$-\log K$	μ	$-\log K + 0.986\sqrt{\mu}$	$1.661 + 0.927\mu$	$\delta \times 10^3$
0.2007	0.001280	0.1654	0.0398	1.400	0.2016	1.844	1.848	−4
0.1000	0.002067	0.2671	0.0364	1.438	0.1015	1.757	1.755	+2
0.0501	0.003065	0.3960	0.0328	1.484	0.0523	1.710	1.709	+1

TABLE 8

K_0 and k^* for nitroisobutyric acid nitroacetic acids

ACID	K_0		k^*		Q
	At 17.84°C	At 9.78°C	At 17.84°C	At 9.78°C	
					kg-cal
Nitroisobutyric acid	0.0118	0.0135	0.0448	0.01395	32.7
Nitroacetic acid	0.0208	0.0218	0.0246	0.00774	23.5

secutive reaction. Here there is a linear relation between $-\log K + A\sqrt{\mu}$ and μ down to the greatest dilution (0.3 − 0.01 M). The last column in tables 4 to 7 shows the agreement of the experimental results for nitroisobutyric and nitroacetic acids with expression 8, using the values of K_0 and B computed in this way. δ is the difference $(-\log K + A\sqrt{\mu}) - (-\log K_0 + B\mu)$.

Table 8 gives the dissociation constants K_0 and the velocity constants

k^* for the two acids. In the last column is given the heat of activation (Q kg-cal.) calculated from k^* in the usual way.

THE VELOCITY OF BROMINATION OF NITROISOBUTYRIC ACID

In the explanation given in the schemes 1 and 2 it is assumed that the decomposition leads directly to the aci-form of the nitro-hydrocarbon. In order to test this some experiments on the bromination of nitroisobutyric acid were carried out.

The aci-forms of aliphatic nitro compounds are brominated practically instantaneously, while the nitro compounds themselves are not brominated directly. From the work of Junell (4) we know that secondary nitropropane is brominated extremely slowly at 18°C. in a strong acid, the velocity being probably determined by the slow isomerization to the aci-form (see also Pedersen (10)).

TABLE 9

Bromination of nitroisobutyric acid at 17.84°C.

IN 0 0998 M HCl				IN 0 0101 M HCl + 0 0900 M NaCl			
t	$c \times 10^3$	$x \times 10^3$	ak^*	t	$c \times 10^4$	$x \times 10^3$	ak^*
10 7	7 340	1 18	0 00711	2 8	7 181	1.186	0 0280
19 8	8 002	2 212	0 00710	8 8	5 808	2 49	0 0276
35 6	7 271	3 260	0 00726	17 1	5 324	3.49	0 0270
46 5	8 110	4 375	0 00724				
56	7 293	4 451	0 00730	Mean value.			0 028
82	7 425	5 495	0 00714	(Indirectly from decomposition experiments...			0 028)
105 5	7 967	6 557	0 00713				
Mean value..			0 0072				
(From decomposition experiments..			0 0074)				

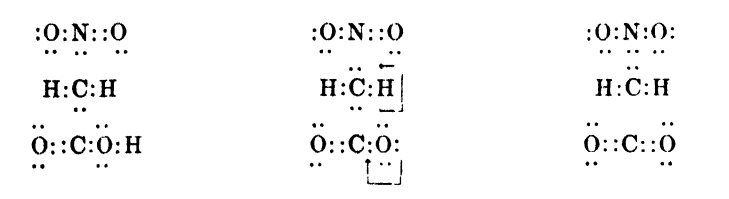
If the explanation expressed in the schemes 1 and 2 is true, the secondary nitropropane should be brominated as soon as it is formed. Thus it should be possible to determine the velocity of decomposition of the nitroisobutyric acid by measuring the velocity of disappearance of the bromine, when the acid is dissolved in bromine water.

To 0.0998 M hydrochloric acid containing bromine at 17.84°C. in a flask with glass stopper was added a known excess of nitroisobutyric acid. The time t which elapsed between the addition of the substance and the disappearance of the brown color was determined. In different experiments with the same concentration of hydrochloric acid and nearly the same initial concentration, c, of nitroisobutyric acid the time of reaction was varied by varying the concentration of bromine. The decrease in the molar concentration of bromine during the time t serves as a measure of the

decrease x in concentration of nitroisobutyric acid. In table 9 the unimolecular velocity constant $\alpha k^* = \frac{1}{t} \log \frac{c}{c-x}$ has been calculated. The mean value $\alpha k^* = 0.0072$ is in agreement with the constant $\alpha k^* = 0.0074$ found by measuring the gas pressure for the same concentration of hydrochloric acid.

In the bromination experiments we avoid the troublesome secondary reaction. It is of interest to do experiments in a solution where the secondary reaction made it impossible to determine directly the velocity constant of the carbon dioxide cleavage. In 0.0101 M HCl + 0.0900 M NaCl the velocity constant of the bromination $\alpha k^* = 0.028$ was found (table 9). In order to compare this result with those for the gas evolution experiments we make the following calculation. From experiments in more acid solution we know that $K = 0.0200$, when $\mu = 0.1$. The hydrogen-ion concentration is $(H^+)_\infty = 0.0101$, when $t = \infty$, and $(H^+)_0 = 0.010 + 0.004 = 0.014$, when $t = 0$, or in average $(H^+) = 0.012$. Hence we find $\alpha = 0.0200/0.032 = 0.62$ and $\alpha k^* = 0.62 \times 0.0448 = 0.028$, in good agreement with the bromination experiments. This shows that the impossibility of determining the constant directly by the pressure method in the most dilute solutions of hydrochloric acid actually is due to a secondary reaction.

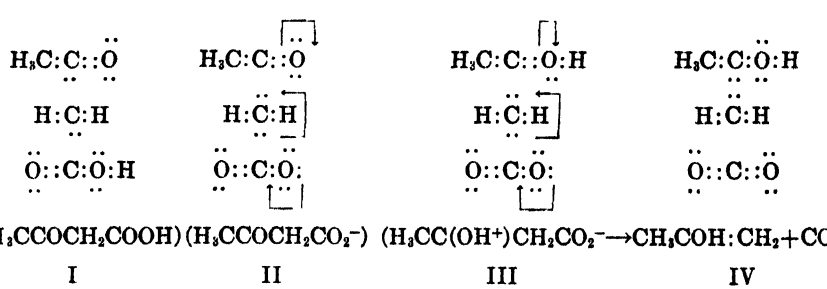
We have now seen that the carbon dioxide cleavages of nitroacetic and α-nitroisobutyric acids follow the same laws. In both cases the undissociated acid is stable, while the univalent ion is decomposed. The velocities are of the same order of magnitude and the heats of activation are the same. From this we may conclude that the unstable form of α-nitrocarboxylic acids in general is not the aci-form of the nitro compound, but the ordinary ion $>CNO_2CO_2^-$. The decomposition leads directly to the aci-form of the corresponding nitrohydrocarbon. From these facts we may try to form a picture of the details of the decomposition. The reaction may be expressed as follows by means of electron valency formulas. It is suggested that the decomposition is caused by a displacement of valency electrons in the direction shown by the arrows.



THE DECOMPOSITION OF β-KETOCARBOXYLIC ACIDS

It is interesting to compare the α-nitrocarboxylic acids with another group of unstable acids, the β-ketocarboxylic acids. The simplest acid of this type, acetoacetic acid, has mainly been examined by Widmark (12, 13) and Ljunggren (5). Here the undissociated acid decomposes with considerable velocity ($CH_3COCH_2COOH \rightarrow CH_3COCH_3 + CO_2$), while the ion decomposes very slowly. The reaction is catalyzed by primary amines. Secondary amines have a small and tertiary amines hardly any effect. From the work on acetoacetic acid it was impossible to decide whether the keto or enol form is active. By studying α,α-dimethylacetoacetic acid, which can not be rearranged into an enol form, Pedersen (8) found that the keto form is unstable. To this can now be added the following result. By making kinetic experiments on the bromination of α,α-dimethylacetoacetic acid in the same way as described above for nitroisobutyric acid and comparing them with earlier experiments on the rate of evolution of carbon dioxide, it was found that bromine is taken up with the same velocity as the keto acid is decomposed (one mole of bromine per mole of keto acid). From these experiments we may conclude that the decomposition of β-ketocarboxylic acids leads directly to the enol form of the reaction product. Thus, there seems to be a close analogy between the mechanism of decomposition of α-nitrocarboxylic acids and β-ketocarboxylic acids.

For β-ketocarboxylic acids we may tentatively suggest the following mechanism. The ordinary form of the undissociated acid (I) is stable. The acetoacetate ion (II) decomposes very slowly. Owing to the weak basic properties of the keto group it will to a small extent take up hydrogen ions. The concentration of the ampho ion (III) thus formed is proportional to the concentration of the ordinary undissociated acid. Consequently it is impossible to decide from the kinetic experiments which of them is unstable. Owing to the attraction of the positive charge it is reasonable to assume that the ampho ion decomposes much more quickly than the ion (II). By the decomposition we get the enol form of the reaction product (IV).



In order to explain the amine catalysis we assume that an equilibrium of the type

$$> CO + H_2NR \rightleftarrows > CNR + H_2O \qquad (9)$$

is quickly established. The group CNR has much stronger basic properties than the keto group. Although the substance >CNR may only be formed in very small concentration by equilibrium 9, we may get a greater concentration of ampho ion than before, and a quicker decomposition.

SUMMARY

This paper contains a kinetic study of the decomposition of α-nitroisobutyric and nitroacetic acids at 17.84°C. and 9.78°C. in acetate buffer solutions and in hydrochloric acid of different concentrations.

From the results it is concluded that the carbon dioxide cleavage of the α-nitrocarboxylic acids consists of a decomposition of the ion with a negative charge at the carboxyl group and leads directly to the aci-form of the corresponding nitro hydrocarbon

$$> C(NO_2)CO_2^- \rightarrow > CNO_2^- + CO_2$$

The dissociation constants of the two acids have been calculated from the kinetic experiments.

The analogy between the carbon dioxide cleavage of the α-nitrocarboxylic acids and the β-ketocarboxylic acids has been pointed out. An attempt has been made to suggest a mechanism which explains the decomposition of both groups of acids and the amine catalysis of the cleavage of the keto acids.

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AN ELECTROMETRIC STUDY OF THE PRECIPITATION OF MERCUROUS HYDROXIDE

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Britton and Robinson (5) find in some cases of the precipitation of the hydroxide or a basic salt from a salt solution by sodium hydroxide, that the reaction is governed by the solubility product of the hydroxide, calculated from the titration curve, whereas in other cases the solubility product so calculated is far from constant.

They include in their paper one curve for the precipitation of a basic nitrate from a solution of mercurous nitrate acidified with nitric acid, by the addition of sodium hydroxide, using the glass electrode as an indicator electrode, but they have not attempted to calculate the solubility product in this case. Accordingly, the work to be described was undertaken and the precipitation of a basic nitrate from acid mercurous nitrate solutions of three different concentrations was studied, the solubility product of mercurous hydroxide being calculated from the titration curves obtained. Three fairly concordant values of the solubility product of mercurous hydroxide have already been published (1, 6, 8), and the reaction seems a very suitable one to test the statement of Britton and Robinson (5) that the solubility product principle is untenable in the case of the precipitation of basic precipitates generally.

EXPERIMENTAL

Preparation and analysis of the solutions

Pure mercurous nitrate was used in this work, and was dissolved in cold water with the addition of sufficient pure dilute nitric acid to prevent the separation of a basic salt. The solution was analyzed before use. Mercury was determined by titration with thiocyanate (7) and total nitrate by reduction to ammonia in caustic soda solution with Devarda's alloy and titration of the ammonia distilled off (10).

pH values of solutions

An attempt was made to use the quinhydrone electrode for the determination of the pH values of the solutions, as this electrode has been stated to behave normally in dilute nitric acid solutions (2), but in all cases tried

it was found to give low readings. Thus in one titration the quinhydrone electrode indicated a pH of 3.0, and the pH values of parallel solutions by the colorimetric and glass electrode methods were 4.1 and 4.05, respectively. It is possible that the quinhydrone electrode is affected by the mercurous–mercuric potential set up at the platinum electrode. After a number of trials the quinhydrone electrode was abandoned in favor of the glass electrode, which has been examined by Britton and Robinson and found suitable for studying precipitation reactions.

The electrode used was of the bulb type filled with normal hydrochloric acid saturated with quinhydrone. It was mounted in a waxed cork supported on an insulated stand, and it dipped into the solution contained in a beaker, the contents being agitated by a mechanical stirrer and connected by means of a saturated potassium nitrate bridge to a saturated calomel electrode. The E.M.F. of the cell was measured with a valve electrometer of standard type used with external potentiometer, both supplied by the Cambridge Instrument Co.

A number of electrodes provided for use with the instrument were examined, using the universal buffer of Britton and Robinson (4), plotting pH against the E.M.F. of the cell. The electrodes all gave a graph differing very little from a straight line, but the sensitivities varied considerably. The most sensitive electrode was used for the work to be described and was standardized using $N/20$ potassium hydrogen phthalate and $N/20$ borax before each titration, a calibration curve being constructed from which the pH could be read off direct. This particular electrode possessed a sensitivity of 0.057 volt per pH unit.

Titration

The curves for the three titrations are reproduced in figure 1. A 10-cc. portion of stock mercurous nitrate solution containing 0.0367 g. of mercury and 0.0320 g. of total nitrate was added to 200 cc. of water and titrated with 1.213 $N/50$ sodium hydroxide to give curve I, and 20-cc. and 30-cc. portions of the same solution with 200 cc. of water were used for curves II and III, respectively. The precipitation was carried out at room temperature, 18°C.

Equilibrium was quickly reached after each addition of alkali, in most cases within two minutes, but longer time was allowed at the bends. Some precipitation took place at the beginning of the titration; most of the precipitate dissolved on prolonged stirring, but the solution remained opalescent. The bulk of the precipitation took place however after the first bend at J′, K′, and L′. That precipitation was complete after the final bend was shown by filtering the solution, evaporating to small bulk, faintly acidifying, and testing for absence of mercury with hydrogen sulfide.

The initial pH of precipitation is higher than that given by Britton and

Robinson (5), which is approximately 3.0, but their solutions were much more concentrated than those used by the author and precipitation would be expected to occur at a lower pH in such solutions. The pH values at the completion of precipitation were 4.84, 4.88, and 4.92; the pH value of

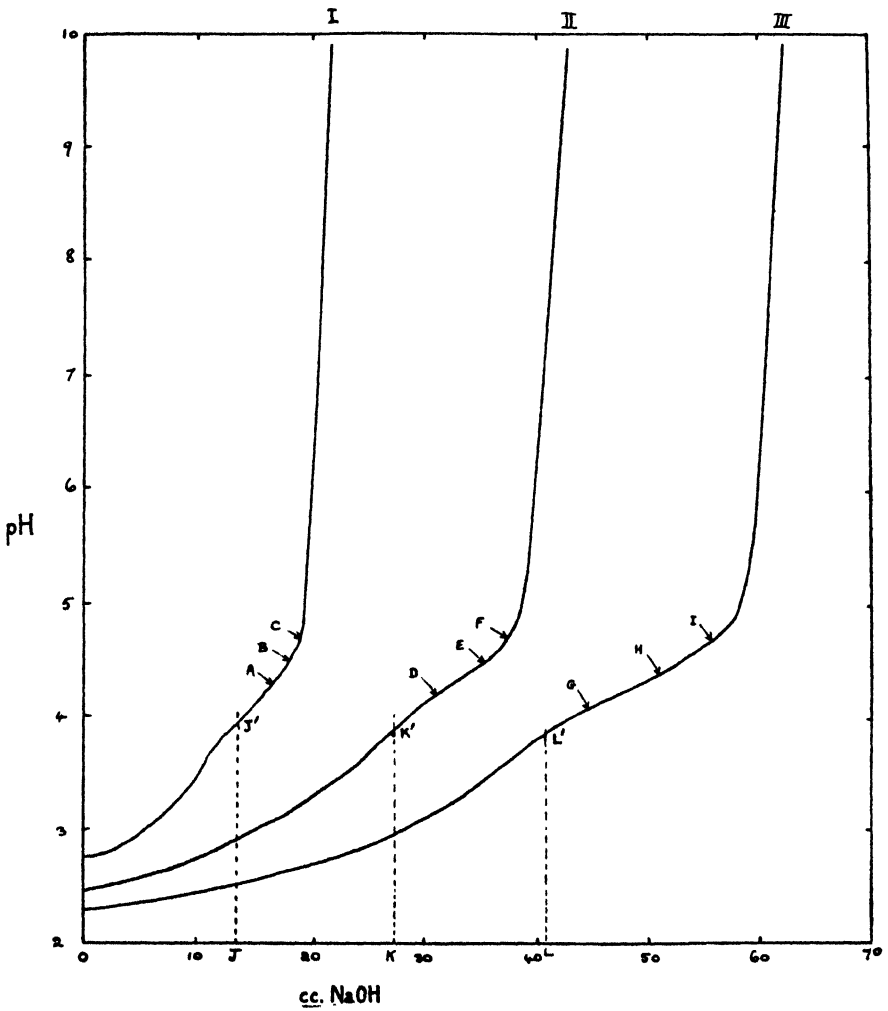

FIG. 1. CURVES FOR THE TITRATIONS

practically complete precipitation of mercurous hydroxide can thus be taken as 4.9.

COMPOSITION OF THE PRECIPITATE

From the analytical figures for total NO_3 and Hg in the solution the amount of free HNO_3 was calculated and the theoretical volume of alkali

required to neutralize the latter. The points J, K, and L indicate the theoretical points of neutralization of the free acid. There are slight inflections of the curves corresponding to these points, but they are much too gradual to fix the points by means of the curves. The difference between the calculated volume of alkali required to neutralize the free acid and the observed amount needed for precipitation, read off from the curve, gives the amount needed for the precipitation of mercurous hydroxide. In all three cases this was less than the theoretical, the ratios of observed to theoretical being 0.722, 0.755, and 0.766. The calculations are set out in table 1.

This would appear to indicate that a basic nitrate of the approximate composition $3Hg_2O \cdot 2HgNO_3 \cdot xH_2O$ was being precipitated, in which the molecular ratio of Hg to NO_3 was 4:1. That this was indeed the composition of the precipitate was proved by conducting a duplicate precipitation using the same amounts of solutions as in experiment III and determining

TABLE 1

Sodium hydroxide required

	Curve I	Curve II	Curve III
Actual NaOH required to react with $HgNO_3$ and HNO_3	19 0 cc.	38 5 cc.	58 0 cc.
Theoretical NaOH required for HNO_3	13 6 cc.	27.2 cc.	40 8 cc.
Actual NaOH required for $HgNO_3$	5 4 cc.	11 3 cc.	17.2 cc.
Theoretical NaOH required for $HgNO_3$	7 48 cc.	14.96 cc.	22.44 cc.
Ratio of observed to theoretical	0 722	0.755	0 766

the total NO_3 in the solution at the end of the titration. All the Hg in the solution had been precipitated and it was thus possible to calculate the amount of NO_3 combined with the Hg. This calculation gave a molecular ratio of Hg to NO_3 in the precipitate of 4.1:1, in good agreement with the value of 4:1 obtained from $3Hg_2O \cdot 2HgNO_3 \cdot xH_2O$. This is more basic than any definite basic nitrate which has been described (9), and it is probable that the precipitate produced is a mixture of a less basic nitrate and mercurous oxide or hydroxide.

CALCULATION OF THE SOLUBILITY PRODUCT

Britton (3) has shown that the pH values necessary for the precipitation of a large number of basic salts from metallic salt solutions, differ very little from the pH values necessary to precipitate the corresponding hydroxides. It is thus obvious that the solubility product of the hydroxide is the predominant factor in the precipitation of such basic salts. This is

confirmed by the fact that the solubility product $[Hg_2^{++}]^2 [OH^-]^3 [NO_3^-]$ corresponding to the basic salt $(Hg_2)_2NO_3(OH)_3$ is less constant than that of the hydroxide, and assuming the above, it is possible to calculate the solubility product of mercurous hydroxide from the curves above described. A method of calculation similar to that used by Britton and Robinson (5) is used. Three points on each curve were arbitrarily chosen (points A, B, C, D, E, F, G, H, I). Knowing the volume of alkali required for complete precipitation, the $[Hg_2^{++}]$ still in solution could be calculated at each point. From the pH, the $[OH^-]$ can be calculated, taking the ionic product of water as 0.73×10^{-14} at 18°C. Thus $[Hg_2^{++}] [OH^-]^2$ can be obtained. The calculations are set out in table 2.

TABLE 2

Calculation of the solubility product

POINT ON CURVE	pH	$[H^+] \times 10^4$	$[OH^-] \times 10^{10}$	NaOH ADDED AT POINT CHOSEN	$[Hg_2^{++}]$ AT BEGINNING OF TITRATION $\times 10^3$	$[Hg_2^{++}]$ AT POINT CHOSEN $\times 10^3$	$[Hg_2^{++}] [OH^-]^2 \times 10^{24}$
				cc			
A	4.3	0.50	1.46	16.7		0.1718	3.6
B	4.5	0.32	2.28	18.0	0.4356	0.0743	3.9
C	4.7	0.20	3.65	18.8		0.0148	2.0
D	4.2	0.63	1.16	31.0		0.4837	6.5
E	4.5	0.32	2.28	35.4	0.8317	0.1965	10.2
F	4.7	0.20	3.65	37.3		0.0755	10.1
G	4.1	0.80	0.913	44.7		0.7720	6.4
H	4.4	0.40	1.83	51.2	1.1933	0.3860	12.9
I	4.7	0.20	3.65	56.0		0.1116	14.9
Mean solubility product							7.8×10^{-24}

It will be observed that the solubility product obtained is not constant, but having regard to the fact that a basic nitrate is actually precipitated and to the presence of sodium nitrate in the solution, the product is sufficiently constant to show that the reaction is governed by it. Other determinations of the solubility product of mercurous hydroxide have been made by Bugarsky (6), Immerwahr (8), and Allmand (1), who obtain the values 1.82×10^{-24}, 8.05×10^{-24}, and 4.8×10^{-24}, respectively. The mean of the values obtained from table 2 is 7.8×10^{-24}, in reasonable agreement with those above. It is quite obvious in this particular case that the titration curve does provide a means of calculating the solubility product of the hydroxide, although a high degree of accuracy cannot be expected.

The constancy of the solubility product is not improved by correcting for the "activities" of the ions and the total ionic strength of the solutions.

HYDROLYSIS

It is well known that considerable hydrolysis occurs in mercurous nitrate solutions, but no direct determination of the extent of the hydrolysis has been made, owing to the difficulty of obtaining the $[H^+]$ in such solutions. The glass electrode renders this determination possible; accordingly the hydrolysis of mercurous nitrate in the three solutions used for the titration, all of which contain free nitric acid, was calculated. In order to simplify the calculation it was assumed that the free nitric acid was completely ionized,—a justifiable assumption having regard to the dilute solutions used. The salt effect of the mercurous nitrate on the pH of the solution was also neglected. The figures are set out in table 3, and it will be seen that even in the presence of a considerable excess of free nitric acid,

TABLE 3
Hydrolysis of mercurous nitrate

SOLUTION	INITIAL pH	$[H^+] \times 10^3$	CALCULATED $[H^+]$ DUE TO $HNO_3 \times 10^3$	$[H^+]$ DUE TO HYDROLYSIS $\times 10^3$	$[NO_3^-]$ FROM $HgNO_3 \times 10^3$	PER CENT OF HYDROLYSIS
I	2.73	1.95	1.58	0.37	0.87	42 5
II	2.44	3.60	3.02	0.58	1.66	34 9
III	2.30	5.00	4.34	0.66	2.39	27.6

hydrolysis is very marked, decreasing with an increase in the total concentration of nitric acid and mercurous nitrate.

SUMMARY

1. The quinhydrone electrode gives high readings in dilute nitric acid solutions of mercurous nitrate. The glass electrode may be used in such solutions.

2. When dilute sodium hydroxide is added to dilute nitric acid solutions of mercurous nitrate, a basic nitrate is precipitated having the approximate composition, $3Hg_2O \cdot 2HgNO_3 \cdot xH_2O$.

3. The precipitation is governed by the solubility product of mercurous hydroxide, which is calculated to be 7.8×10^{-24}.

4. Mercurous nitrate is hydrolyzed to a considerable extent in the dilute nitric acid solutions studied.

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THE THEORY OF PROTOLYTIC REACTIONS AND PROTOTROPIC ISOMERIZATION

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According to Brönsted's (3) definition of acids and bases any neutral molecule or ion which can give off a proton is called an acid, and any neutral molecule or ion which can take up a proton is called a base. When

$$A \rightleftarrows B + H^+$$

A is an acid and B the corresponding base. Lowry (27) has independently suggested the same definition. The proton being incapable of independent existence, an acid can only give off a proton to a base. Thus the characteristic acid and base function is the transference of protons from the acid to the base as expressed in the scheme

$$A_1 + B_2 \rightleftarrows B_1 + A_2 \tag{1}$$

where the base B_1 corresponds to the acid A_1, and the acid A_2 to the base B_2. Brönsted (6) calls this a protolytic reaction.

The relative strength of two acids or bases is defined by means of the degree of displacement of equilibrium 1. If K_A is the strength of an acid A and K_B that of a base B, we use the definition

$$\frac{K_{A_1}}{K_{A_2}} = \frac{K_{B_2}}{K_{B_1}} = \frac{(B_1)(A_2)}{(A_1)(B_2)} \tag{2}$$

In this way we can compare the strengths of two acids or bases in any solvent. The relative strength is usually dependent on the solvent. If the solvent S is a base we get the equilibrium

$$A_1 + S \rightleftarrows B_1 + SH^+$$

In this case we define the strength of the acid A_1 and the base B_1 in the solvent by

$$K_{A_1} = \frac{1}{K_{B_1}} = \frac{(SH^+)(B_1)}{(A_1)} \tag{3}$$

Where there can be no misunderstanding we often call the ion SH^+ the hydrogen ion and denote it by H^+. In the solvent water SH^+ is the hydroxonium ion H_3O^+.

Protolytic reactions are generally very rapid. It has not yet been possible to show with certainty that the interaction of ordinary acids and bases takes a finite time. Only the so-called pseudo acids, which will be dealt with later, react in some cases with measurable velocity. By means of the flowing stream method of Hartridge and Roughton (20) it has been shown by Saal (38) that the reaction between hydroxyl ions and different weak acids and between hydrogen ions and different weak bases is complete in less than 0.004 second. La Mer and Read (24) found by the same method that the reaction between 0.05 N solutions of acetic acid and ammonia at 25°C. was only 95 per cent complete 0.002 second after mixing. These authors intend to repeat the experiment with an improved apparatus. It will be of interest to see whether the result will be confirmed.

It is reasonable to assume that the velocity of the protolytic reaction is to some extent determined by the strength of the reacting acid and base. The weaker the acid and base the slower the reaction. However, by purely static considerations we cannot find a relation between the velocity and the strengths of the acid and base. If we denote by v_{A_1, B_2} and π_{A_1, B_2}, respectively, the velocity and the bimolecular velocity constant for the transference of a proton from A_1 to B_2 (scheme 1), we have

$$v_{A_1,B_2} = \pi_{A_1,B_2}(A_1)(B_2) \qquad \text{and} \qquad v_{A_2,B_1} = \pi_{A_2,B_1}(A_2)(B_1)$$

At equilibrium $v_{A_1, B_2} = v_{A_2, B_1}$, and consequently

$$\frac{\pi_{A_1,B_2}}{\pi_{A_2,B_1}} = \frac{(B_1)(A_2)}{(A_1)(B_2)}$$

By means of equation 2 we get the relation

$$\frac{\pi_{A_1,B_2}}{\pi_{A_2,B_1}} = \frac{K_{A_1}}{K_{A_2}} = K_{A_1} \times K_{B_2} \tag{4}$$

Only the ratio between the velocity constants of the balanced reaction 1, not the separate constants, is given by expression 4, which is all we can get in this way. Only kinetic experiments can decide whether the velocity is determined by the strengths of the acid and base.

It has been found, first by Brönsted and his coworkers (7–10, 12–15), afterwards by many other investigators (16, 17, 23, 26, 31, 33, 34, 35, 36, 42), that a great number of reactions are catalyzed by acids or bases in general, that is, all sufficiently strong acids or bases catalyze, and the effect increases with increasing acid or basic strength of the catalyst. Brönsted has developed a theory of this general acid and basic catalysis (4, 5).

According to this theory the velocity is determined by a protolytic reaction between the substrate and the catalyst. We have general acid or basic catalysis if the substrate molecule by receiving or by giving off a proton gets into an unstable state which immediately (or very quickly compared with the velocity of the protolytic reaction) leads to the reaction which we examine. If in acid and basic catalysis we call the substrates R and RH respectively, the velocities are determined by the reactions

$$R + A \rightarrow RH^+ + B \tag{5}$$

and

$$RH + B \rightarrow R^- + A \tag{6}$$

The substrate is an extremely weak base or acid, and since the corresponding acid (RH^+) or base (R^-) disappears practically immediately after its formation, it is possible to follow the protolytic reaction.

If the velocity of the protolytic reaction is determined mainly by the strengths of the reacting acid and base while other factors have a minor influence, by plotting the catalytic constants (k_A for the acid catalyst A, and k_B for the basic catalyst B) for a series of catalysts of the same reaction against the acid or basic strength, we should get points which fall not far from a continuous curve. Actually it has been found for a great number of reactions that the points fall very close to a straight line when log k_A is plotted against log K_A and log k_B against log K_B. Thus it follows from the experiments that we may express the dependence of the catalytic constant upon the strength of the catalyzing acid or base by the equations

$$k_A = \pi_{A,R} = gK_A{}^{\alpha} \tag{7}$$

and

$$k_B = \pi_{RH,B} = gK_B{}^{\beta} \tag{8}$$

The influence of the strength of the catalyzing acid or base is expressed by K_A^{α} or K_B^{β} respectively, where α and β are constants characteristic of the reaction examined. The factor g usually does not vary much within a series of acid or basic catalysts of the same reaction. For the transference of a proton from RH^+ to B we get by means of equation 4

$$\pi_{RH^+,B} = \frac{\pi_{A,R}}{K_A \times K_R} = gK_{RH^+} \times K_B{}^{1-\alpha}$$

If we assume that an increase of K_A tends to increase $\pi_{A,R}$ while an increase of K_B tends to increase $\pi_{RH^+,B}$, both α and $1-\alpha$ must be positive, that is $0 < \alpha < 1$. In the same way we find that $0 < \beta < 1$. These results are in agreement with the experiments.

STATISTICAL FACTORS (CF. BRÖNSTED (4, 5, AND 12))

The number of protons which an acid molecule can give off and the number of vacant places on a base molecule where a proton can be taken up has an influence on the velocity of transference of a proton from the acid to the base, and therefore on g in the expressions 7 and 8. We assume that $g = G$ when A can give off only one proton and B can take up only one proton. We shall compare this simple case with a more general one where A has p protons, each bound with the same strength as in the simple case, and B has q vacant places, each with the same tendency to take up a proton as in the simple case. It is a necessary, though not sufficient, condition for a transference of a proton from A to R that the active part of the molecule R hits A within a certain area round a proton which can be given off. If we assume that the active areas of A do not overlap, $\pi_{A,R}$ will be p times as great as in the simple case. We find in the same way, when we assume that the active areas of B do not overlap, that $\pi_{RH^+,B}$ will be q times as great as in the simple case. By means of equation 4 we find that K_A will be p/q times as great. Consequently we get

$$\frac{k_A}{p} = G\left(\frac{p}{q}K_A\right)^{\alpha} \tag{9}$$

or $g = p^{1-\alpha}\, q^{\alpha}\, G$. By similar considerations we find for basic catalysis

$$\frac{k_B}{q} = G\left(\frac{p}{q}K_B\right)^{\beta} \tag{10}$$

or $g = q^{1-\beta}\, p^{\beta}\, G$.

It seems reasonable to assume that more protons bound to the same atom in an acid count as one when determining the statistical factor. Thus $p = 1$ for H_3O^+ and NH_4^+, while $p = 2$ for H_2SO_4. Similarly, when a base can take up more protons at the same atom, this place is only counted as one. Thus $q = 2$ for $CH_3CO_2^-$ and $q = 1$ for OH^-.

THE INFLUENCE OF THE ELECTRIC CHARGE OF THE CATALYST

The value of g in equations 7 and 8 depends on the electric charge of the catalyst. Let us consider basic catalysis and only reactions where the substrate RH is uncharged. We assume that equation 8 holds for a series of bases with no electric charge when g has the value g_0, and for a series of bases with one negative charge when $g = g_-$. We now consider two hypothetical bases B^- and B differing only in their electric charge. We compare the reactions

$$RH + B^- \rightleftarrows R^- + BH \tag{11}$$

and

$$RH + B \rightleftarrows R^- + BH^+ \tag{12}$$

We assume that β in equation 8 is independent of the charge. We have

$$k_B = g_0 K_B{}^{\beta} \quad \text{and} \quad k_{B^-} = g_- K_{B^-}{}^{\beta}$$

Hence

$$\frac{g_0}{g_-} = \frac{k_B}{k_{B^-}} \left(\frac{K_{B^-}}{K_B}\right)^{\beta} \tag{13}$$

We have

$$\frac{k_B}{k_B} = \frac{\pi_{RH,B}}{\pi_{RH,B^-}}, \quad K_B = \frac{\pi_{RH,B}}{\pi_{BH^+,R^-}}, \quad \text{and} \quad K_{B^-} = \frac{\pi_{RH,B^-}}{\pi_{BH,R^-}}$$

which we introduce into equation 13. Hence

$$\frac{g_0}{g_-} = \left(\frac{\pi_{RH,B}}{\pi_{RH,B^-}}\right)^{1-\beta} \left(\frac{\pi_{BH^+,R^-}}{\pi_{BH,R^-}}\right)^{\beta} \tag{14}$$

In going from reaction 11 to 12 the velocities change in the following way. It will be more difficult for B to take up a proton than for B^-, but it will be easier for BH^+ to give off one than for BH, and, in addition to this effect, the electric attraction between BH^+ and R^- will increase the velocity of the reaction from right to left. From this we conclude that the following relation will probably hold

$$\frac{\pi_{BH^+,R^-}}{\pi_{BH,R}} > \frac{\pi_{RH,B^-}}{\pi_{RH,B}} > 1$$

By introducing this into equation 14 we find, that $g_0 < g_-$ when β is very small, and $g_0 > g_-$ if β is sufficiently great and always if $\beta > 1/2$.

The influence of more negative charges can be examined in the same way. For a base with two negative charges ($g = g_{--}$), we find that $g_{--} > g_-$ when β is very small, and $g_{--} < g_-$ when β is sufficiently great and always if $\beta > 1/2$.

If we compare bases of the same strength we may express the effect of the electric charges as follows. The base with the greatest number of positive charges (smallest number of negative charges) is the strongest catalyst, when β is sufficiently great, and always if $\beta > 1/2$. The greater β, the greater the effect. When β is very small the effect goes in the opposite direction. The attraction between R^- and a positive ion is greater and increases more rapidly with increasing electric charge of the ion than the repulsion between R^- and a negative ion, the former being on the average nearer together than the latter. Consequently, the effect will increase more rapidly in the series B^-, B, B^+, B^{++} . . . than it will decrease in the series B^-, B^{--} . . . .

For acid catalysis we find analogous rules. Among acids of the same strength the strongest catalyst is the one with the greatest number of

negative charges (smallest number of positive charges), when α is sufficiently great, and always if $\alpha > 1/2$. When α is very small the effect is opposite. The effect will increase more rapidly in the series A^+, A, A^-, A^{--} . . . than it will decrease in the series A^+, A^{++} . . . .

THE SALT EFFECT

Addition of salt will generally alter both the velocity constant (k_A or k_B) and the strength (K_A or K_B) of the catalyzing acid or base. When the substrate is uncharged the primary (5, 12) kinetic salt effect is generally small, but there is a considerable salt effect on K_A (except when A has one positive charge) and on K_B (except when B is uncharged). Therefore we may expect to get a better agreement with experiment when in formulas 9 and 10 we use, instead of K_A and K_B, their values at infinite dilution, K_A^0 and K_B^0:

$$\frac{k_A}{p} = G\left(\frac{q}{p}K_A^0\right)^\alpha \tag{15}$$

and

$$\frac{k_B}{q} = G\left(\frac{p}{q}K_B^0\right)^\beta \tag{16}$$

If the substrate molecule is charged it is very important not to neglect the different effect of salts on the velocity and on the acid and basic strength.

As an example of the application of the theory we shall give a summary of experiments on the decomposition of nitramide in aqueous solution at 15°C.

$$H_2N_2O_2 \rightarrow N_2O + H_2O$$

It was through the study of this reaction that general basic catalysis was first found (Brönsted and Pedersen (12)). The work has been continued by Brönsted and Duus (8) and by Brönsted and Volqvarts (14). Recently Brönsted and Vance (13) have examined the reaction in amyl alcohol.

Acids have no catalytic effect on the decomposition of nitramide in aqueous solution. In dilute solutions of strong acids a slow reaction with the unimolecular constant $k_0^* = 0.00038$ min.$^{-1}$ was found. (By an asterisk we denote that the constant has been calculated by means of decadic logarithms. Thus $k^* = 0.4343k$.) This so-called spontaneous reaction is simply explained as basic catalysis by the water. In solution containing bases B the velocity constant can be written $k = k_0 + \Sigma k_B(B)$ or, if we consider the water as a base of the concentration 55.5 and write $k_{H_2O} = k_0/55.5$, in the simpler way $k = \Sigma k_B(B)$.

Since the publication of the first paper our views on the effect of statistical factors have altered somewhat. Here the results have therefore been

recalculated in accordance with formula 16. We have also in some cases deviated from the original papers in the determination of the statistical

TABLE 1

The decomposition of nitramide at 15°C.

	CATALYST	p	q	k_B^*	$\log \frac{k_B^*}{q}$	$\log \frac{p}{q} K_B^0$	$G^* \times 10^5$
Bases with one negative charge $\beta = 0.80$ $G^* = 7.2 \times 10^{-5}$	Propionate ion	1	2	0 649	0.51–1	4 57	7.1
	Acetate ion	1	2	0.504	0 40–1	4 44	7 1
	Acid succinate ion	2	2	0 320	0.20–1	4 19	7.1
	Phenylacetate ion	1	2	0 232	0 06–1	3 98	7.6
	Benzoate ion	1	2	0.189	0.97–2	3.89	7 2
	Formate ion	1	2	0.0822	0.61–2	3.38	8 1
	Acid malate ion	2	2	0 0765	0.58–2	3.40	7.2
	Acid tartrate ion	2	2	0 0363	0 26–2	3 01	7 1
	Acid phthalate ion	2	2	0 029	0 16–2	2 92	6 6
	Salicylate ion	1	2	0 0206	0 01–2	2.70	7 1
	Primary phosphate ion	3	2	0 0079	0 60–3	2 30	(5.8)
	Dichloroacetate ion	1	2	0 0007	0.54–4	1.00	(5.5)
Bases with two negative charges $\beta = 0.87$ $G^* = 2.07 \times 10^{-5}$	Secondary phosphate ion	2	3	86	1 46	7 06	2 09
	Normal succinate ion	1	4	1 8	0 66–1	5 02	1 95
	Normal malate ion	1	4	0 72	0.26–1	4.51	2 19
	Normal tartrate ion	1	4	0.165	0.62–2	3.79	2 09
	Normal oxalate ion	1	4	0.104	0.42–2	3 57	2 04
Bases with no charge $\beta = 0.75$ $G^* = 17.0 \times 10^{-5}$	*p*-Toluidine	1	1	1.16	0.06	5 15	15 8
	m-Toluidine	1	1	0 64	0 81–1	4.82	15 5
	Aniline	1	1	0 54	0 73–1	4 70	16.2
	o-Toluidine	1	1	0 38	0.60–1	4 54	15.8
	p-Chloroaniline	1	1	0 21	0 32–1	4 04	19.5
	m-Chloroaniline	1	1	0.081	0.91–2	3.52	18 6
	o-Chloroaniline	1	1	0 018	0.26–2	2.68	17.8
	Water	1	1	$6\ 8 \times 10^{-6}$	0.85–6	−1.74	(14)
Bases with two positive charges $\beta = 0.82$ $G^* = 780 \times 10^{-5}$	$[Rh(NH_3)_5(OH)]^{++}$	1	1	396	2 598	5 86	620
	$[Co(NH_3)_5(OH)]^{++}$	1	1	449	2 652	5.69	980
	$[Co(NH_3)_4(H_2O)(OH)]^{++}$	2	1	328	2 516	5.52	1000
	$[Co(NH_3)_3(H_2O)_2(OH)]^{++}$	3	1	135	2.130	5 20	740
	$[Al(H_2O)_5(OH)]^{++}$	6	1	121	2 083	5.73	(240)
	$[Cr(H_2O)_5(OH)]^{++}$	6	1	32.7	1.515	4.68	480
	$[Fe(H_2O)_5(OH)]^{++}$	6	1	2 28	0 358	2 98	830

factors by using the rules given above. The strengths of the bases are usually those given in the three papers (8, 12, 14). For the primary and secondary phosphate ion they are taken from the investigation by Bjer-

rum and Unmack (2), and for the succinate, malate, tartrate, and oxalate ion from Larsson's measurements (25).

A study of table 1 and figure 1 will show that there is a good agreement between the theory and the experiments. Formula 16 holds well within a group of bases with the same electric charge. The change of catalytic effect on going from one type of bases to another goes in the direction we

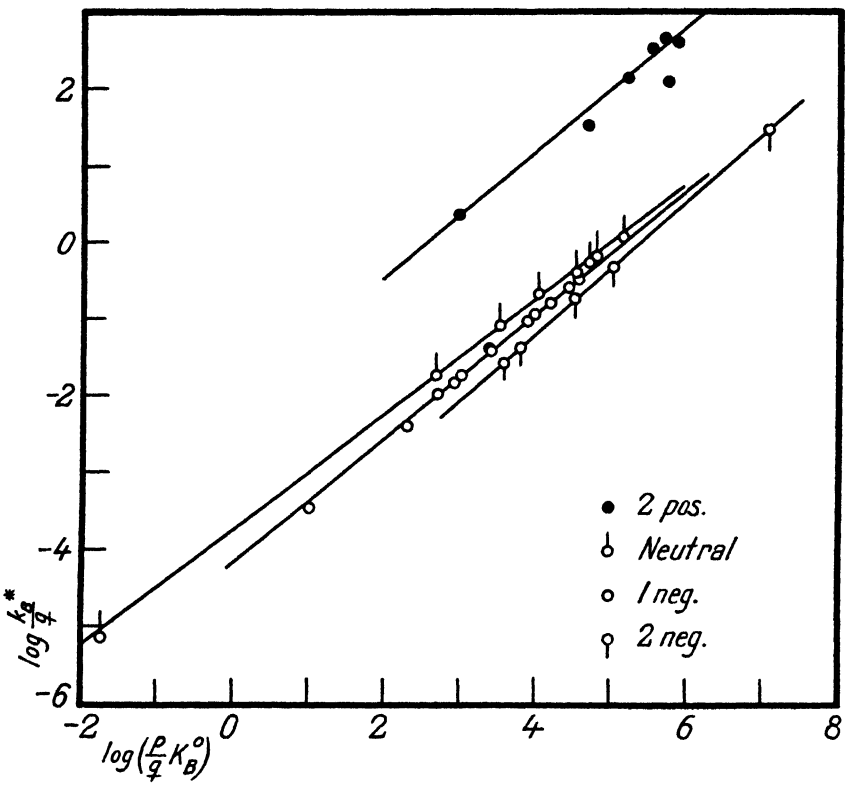

FIG. 1. THE DECOMPOSITION OF NITRAMIDE
Dependence of catalytic constant upon basic strength

would expect. In agreement with the theory, the effect of bases with two positive charges is especially great, about one hundred times as great as of bases with the same strength and one negative charge. The catalysis by water has the order of magnitude we would expect when we use for the basic strength of water the value $K_B = (H_3O^+)/(H_2O)\ (H_3O^+) = 55.5^{-1}$.

Nitramide is a weak acid. Brönsted and King (11) have found by measurements of electrical conductivity that its apparent strength is $K^0 = 2.55 \times 10^{-7}$ at 15°C. It is seen from their measurements that the

protolytic reaction by which the dissociation equilibrium is attained is very much quicker than the decomposition. Therefore the protolytic reaction which leads to decomposition must be another. We assume that the following equilibria are attained practically instantaneously

$$H_2NNO_2 \rightleftarrows HN{:}NO_2^- + H^+ \rightleftarrows HN{:}NOOH$$

Thus a constant, but very small, fraction of the undissociated nitramide is in the form HN:NOOH. We may explain the decomposition as taking place when the last proton bound to the nitrogen atom is given off to the base. This explanation is supported by the fact that nitramines of the type $RHNNO_2$, e.g. methylnitramine, are stable. Thus Thiele and Lachmann (40) have found that methylnitramine undergoes boiling with potassium hydroxide without decomposition. From this fact we may conclude that body hydrogen atoms in nitramide play a part in the decomposition.

It has been found by Brönsted (11, 14) that the nitramide ion is unstable and decomposes about twenty times more quickly than undissociated nitramide in pure water. This is also in conformity with the explanation. Owing to the negative charge of the ion $HN{:}NO_2^-$ the proton is bound much more strongly than the corresponding proton in HN:NOOH, and the protolytic reaction which leads to decomposition will therefore be much slower, but, on the other hand, all the nitramide ion is in the unstable form, while this is only the case with a small fraction of the undissociated nitramide.

For other examples of general basic or acid catalysis we refer to the literature (4, 5, 7–10, 12, 13, 14–17, 23, 26, 31, 33–36, 42).

One of the best known forms of reversible isomerization is that characterized by the change of position in the molecule of a proton, which may be accompanied by a rearrangement of bonds (valency electrons). Lowry (28) has called this form of isomerism prototropy. Although Lowry only considers isomerizations with both proton- and bond-shifting it seems reasonable to include under the name prototropy also those where only proton-shifting takes place, e.g., $H_2NCH_2COOH \rightleftarrows {}^+H_3NCH_2CO_2^-$. However, we shall deal here mainly with the former class of prototropy.

The greatest number of reactions in which general acid or basic catalysis has been found are prototropic isomerizations. Thus the mutarotation of glucose (9, 31) and the enolization of acetone (17) are catalyzed by both acids and bases, while the enolization of acetoacetic ester and acid (35, 36) and the isomerization of nitromethane (34), $CH_3NO_2 \rightarrow CH_2{:}NOOH$, are catalyzed only by bases.

The best examined prototropic systems belong to the triad- or the ring-chain systems, respectively,

$$H{\cdot}X{\cdot}Y{:}Z \rightleftarrows X{:}Y{\cdot}Z{\cdot}H \quad \text{and} \quad (A)\left\langle\begin{array}{l} X \\ | \\ Y{\cdot}Z{\cdot}H \end{array}\right. \rightleftarrows (A)\left\langle\begin{array}{l} X{\cdot}H \\ \\ Y{:}Z \end{array}\right.$$

where X, Y, and Z may be chosen among the three atoms O, N, and C (41). Of the prototropic reactions mentioned above, mutarotation belongs to the latter class, while the others belong to the former.

A great deal of work on prototropic systems has been carried out by Thorpe, Ingold, and their coworkers, although not from the point of view of general acid and basic catalysis. We shall here mention some of their most important results. The hydrogen atom is much more mobile when it goes from one nitrogen atom to another than when it goes from one carbon atom to another, and there is no doubt that it is even more mobile when it goes from oxygen to oxygen. Compared with this the nature of the third atom in the triad Y is of minor importance (21). Thus the mobility increases in the same order as the tendency to give off a proton (methane is a weaker acid than ammonia and this weaker than water). The mobility is dependent on substituents in the prototropic molecule. Electronegative groups, which increase the tendency to give off a proton, increase the mobility (22, 39). The mobility is catalyzed by bases, and in some cases also by acids, although usually to a less extent. The strong bases are the strongest catalysts, in water OH^-, in ethyl alcohol $C_2H_5O^-$, etc.

From work in this field it seems justifiable to conclude that the hydrogen cannot move spontaneously from one place to another in the molecule. If the prototropic equilibrium is apparently attained without catalyst, it has often been possible to show that the reaction is catalyzed by small amounts of acid and basic impurities. Thus, while the keto–enol equilibrium is attained quickly in acetoacetic ester of ordinary purity, Meyer (32) and Rice and Sullivan (37) have shown that the stability of the enol form can be increased apparently without limit by careful purification. Rice and Sullivan found that addition of traces of bases to the purified enol form increased the velocity of isomerization immensely. Thus the addition of 4×10^{-5} *M* ammonia increased it 4000 times, while 10^{-5} *M* oxalic acid increased it only 3.2 times.

The necessity for a catalyst has been shown most clearly by Lowry and Richards (30) for the mutarotation of tetramethylglucose. They even find that both an acid and a base must be present. If the solvent is both an acid and a base, like water, this alone can catalyze the reaction. If it is only an acid or only a base, no reaction can take place, unless we add respectively a base or an acid. Thus the mutarotation takes place with measurable velocity in water and is catalyzed by acids and bases, e.g., cresol and pyridine. In pure and dry pyridine or cresol the reaction is completely arrested, but in a mixture of pyridine and cresol it takes place with great velocity.

Supported by these experiments Lowry has given an explanation of the mechanism of prototropic isomerization in his electrolytic theory of cataly-

sis (29), according to which it is a trimolecular reaction between the substrate, an acid, and a base. The following three things take place simultaneously: (a) the substrate molecule gives up a proton to the base, (b) it receives one in another place from the acid, and (c) a rearrangement of valency electrons takes place. Another mechanism has been suggested by Ingold, Shoppee, and Thorpe (22). They assume that (a) and (b) are consecutive bimolecular reactions. This idea is supported by experimental work of Baker (1).

In order to examine Lowry's explanation we consider the prototropic reaction RH $\rightarrow$ SH in a medium containing the acids A_1, A_2 . . . and their corresponding bases B_1, B_2 . . . . According to Lowry the isomerization is the result of the reaction

$$A_m + RH + B_n \rightarrow B_n + SH + A_n \tag{17}$$

and the analogous reactions with the other acids and bases. If the trimolecular velocity constant of reaction 17 is called k_{A_m, B_n}, we get the following expression for the total velocity

$$v = (RH)\, \Sigma k_{A_m, B_n} (A_m)(B_n) \tag{18}$$

where the sum should be taken for all combinations of m and n. Actually both Lowry's and other investigators' experiments in aqueous solution agree with the formula

$$v = (RH)\Sigma[k_A(A) + k_B(B)] \tag{19}$$

where the sum is taken for all acids and bases present. Expressions 18 and 19 agree only if one of the partners in reaction 17 is always (or nearly always) a solvent molecule, because the solvent is the only catalyzing substance whose concentration has not been varied in the experiments. Thus it follows for aqueous solutions that water is always a partner in the reaction, acting as a base in acid catalysis and as an acid in basic catalysis.

It seems unlikely that this consequence of Lowry's theory is in agreement with experimental facts. Let us consider Dawson's (17) experiments on the enolization of acetone. From his results we calculate the relative velocities of the water, acetate ion, and acetic acid catalysis in an aqueous solution of 0.1 *M* acetic acid and 0.1 *M* sodium acetate. They are given below together with the trimolecular reaction by which that part of the total reaction takes place according to Lowry's theory.

		Relative velocity
Water catalysis	$H_2O + RH + H_2O$	1
Acetate ion catalysis	$H_2O + RH + Ac^-$	61
Acetic acid catalysis	$HAc + RH + H_2O$	18

From a comparison of the first two reactions it is clear that, when RH receives a proton from a water molecule, the amount of acetate ion present

takes up a proton from RH much more quickly than the water does. This will probably also be the case when RH receives a proton from an acetic acid molecule. We would therefore expect the reaction HAc + RH + $Ac^- \rightarrow$ to be quicker than the third reaction in the list. But actually it has not been possible to detect this reaction (cf. formula 19).

We may add that if one of the partners is always water, the acid catalysis of water would always have the same strength as its basic catalysis because both correspond to the same reaction H_2O + RH + $H_2O \rightarrow$. However, some reactions are only catalyzed by bases. Thus the enolization of acetoacetic ester (35, 36) is catalyzed by water and bases, while even the strong acid, the hydroxonium ion, does not catalyze. It, therefore, seems unlikely that the very weak acid water has a considerable power as an acid catalyst.

From this examination we conclude that it is very unlikely that the prototropic isomerization is a trimolecular reaction between the substrate, an acid, and a base. We must therefore assume that the reaction is initiated by a bimolecular reaction in which a proton is either given off to the base or taken up from the acid. Lowry (29) rejects this mechanism for the following reason, using the mutarotation of glucose as an example. "The initial stage in this action is, however, an endothermic process, in which the molecules of the sugar are converted into ions of such an unstable character that the dissociation constant is said to be of the order of 10^{-13} and 10^{-19}. The exact amount of energy required to produce these ions is unknown, but it is obvious that, if we can regard the entrance and the exit of the proton as simultaneous, no energy at all is needed beyond the small amount that is required to cover the difference in energy content of the two isomerides, and perhaps to overcome the frictional resistance to the migration of an electron through the sugar." Lowry seems to forget the part played by the activation energy. This energy is not negligible. Thus Kilpatrick and Kilpatrick (23) found 19.3 kg-cal. for the mutarotation of glucose catalyzed by hydrogen ions.

In the following we shall discuss a mechanism of prototropic reaction based upon the results to which we have now come. It is, especially for basic catalysis, very similar to the mechanism suggested by Ingold, Shoppee, and Thorpe (22).

We assume that an intramolecular rearrangement in which only valency electrons are moved takes place spontaneously and very rapidly. If we as an example consider the triad system $HX \cdot Y:Z \rightleftarrows X:Y \cdot ZH$, the bond-shifting may take place by the following balanced reaction

$$HX \cdot Y:Z \rightleftarrows \overset{+}{H}X:Y \cdot \overset{-}{Z} \quad (RH) \tag{20}$$

$$\overset{-}{X} \cdot Y:\overset{+}{Z}H \rightleftarrows X:Y \cdot ZH \quad (SH) \tag{21}$$

$$\overset{-}{X} \cdot Y:Z \rightleftarrows X:Y \cdot \overset{-}{Z} \quad (I^-) \tag{22}$$

$$HX \cdot Y:\overset{+}{Z}H \rightleftarrows \overset{+}{H}X:Y \cdot ZH \quad (IH_2^+) \tag{23}$$

The equilibria being attained immediately we may consider each pair of tautomers as a single substance, which we may denote as given in brackets above. At first we leave open the question by which of the reactions (20 to 23) the bond-shifting takes place.

We shall see that the prototropic rearrangement RH $\rightleftarrows$ SH appears as a general basic catalysis when the mechanism is as expressed by the scheme

$$\mathrm{RH} + \mathrm{B} \rightleftarrows \mathrm{I}^- + \mathrm{A} \rightleftarrows \mathrm{SH} + \mathrm{B} \tag{24}$$

while it appears as a general acid catalysis when the mechanism is the following

$$\mathrm{RH} + \mathrm{A} \rightleftarrows \mathrm{IH}_2^+ + \mathrm{B} \rightleftarrows \mathrm{SH} + \mathrm{A} \tag{25}$$

We first consider scheme 24. For simplicity we examine an irreversible prototropic isomerization RH $\rightarrow$ SH. We may obtain the one-way reaction by removing the form SH as soon as it is formed. We assume that the medium contains the acids A_1, A_2 . . . and their corresponding bases B_1, B_2 . . . . The concentrations of the acids and bases are constant during the reaction. We may therefore formally consider all the bimolecular reactions of scheme 24 as unimolecular, which simplifies the scheme to

$$\mathrm{RH} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{I}^- \xrightarrow{k_2} \mathrm{SH} \tag{26}$$

where k_1, k_{-1}, and k_2 are unimolecular velocity constants given by the expressions

$$k_1 = \Sigma\pi_{\mathrm{RH,B}}(\mathrm{B}), \qquad k_{-1} = \Sigma\pi_{\mathrm{A,I^-}}(\mathrm{A}) \qquad \text{and} \qquad k_2 = \Sigma\pi''_{\mathrm{A,I^-}}(\mathrm{A})$$

Here $\pi'_{\mathrm{A,\,I^-}}$ denotes the bimolecular velocity constant for that particular transference of protons from A to I^- which leads to RH, while $\pi'_{\mathrm{A,\,I^-}}$ is the constant for the protolytic reaction between A and I^- leading to SH.

If the subscript E denotes equilibrium concentrations, and if K is the constant $(\mathrm{H}^+)_E\,(\mathrm{I}^-)_E/(\mathrm{RH})_E$ we have, according to scheme 26,

$$\frac{(\mathrm{H}^+)_E}{K} = \frac{(\mathrm{RH})_E}{(\mathrm{I}^-)_E} = \frac{k_{-1}}{k_1} \tag{27}$$

We now make the assumption that the hydrogen-ion concentration is so great that $(\mathrm{I}^-) << (\mathrm{RH})$ even if the equilibrium RH $\rightleftarrows$ SH were attained. This is nearly always the case under ordinary experimental conditions. Consequently we have $k_{-1} >> k_1$.

If c is the initial concentration of RH and $c - x$ its concentration at the time t we find, remembering that (I^-) is negligible compared with (RH), the following differential equations for reaction 26,

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1(c - x) - k_{-1}(\mathrm{I}^-) \qquad \text{and} \qquad \frac{\mathrm{d}x}{\mathrm{d}t} = k_2(\mathrm{I}^-)$$

from which we get by eliminating (I^-)

$$\frac{dx}{dt} = \frac{k_1 k_2}{k_{-1} + k_2}(c - x)$$

Thus the reaction follows the ordinary unimolecular law with the constant

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \tag{28}$$

We now distinguish between three cases:

Case 1: $k_{-1} << k_2$. By introducing this into equation 28 we find $k = k_1 = \Sigma\, \pi_{RH,\,B}\,(B)$. In this case we have general basic catalysis. We measure the velocity of transference of protons from RH to B.

Case 2: $k_{-1} >> k_2$. By equations 28 and 27 we get

$$k = \frac{k_1}{k_{-1}} k_2 = \frac{K}{(H^+)} k_2 = \sum \frac{K}{(H^+)} \pi''_{A,I^-}(A) = \sum \frac{K}{K_A} \pi''_{A,I^-}(B)$$

As seen from the last expression the reaction appears to be a basic catalysis of RH, but in reality we measure a general acid catalysis of the ion I^-, whose concentration is inversely proportional to the hydrogen-ion concentration.

Case 3: $k_{-1} \sim k_2$. Here we get from equation 28

$$k = \frac{k_1}{1 + \frac{k_{-1}}{k_2}}$$

The ratio k_{-1}/k_2 is independent of the hydrogen-ion concentration, since k_{-1} and k_2 are independent of the concentrations of the bases, and if we increase the concentrations of all the acids in a certain ratio both k_{-1} and k_2 are increased in the same ratio. Thus, in this case also, the reaction appears as a general basic catalysis. In reality it is composed of a basic catalysis of RH and an acid catalysis of I^-.

We have found that the mechanism expressed in scheme 26 leads to a reaction which will always appear as a unimolecular reaction catalyzed by bases in general, when the hydrogen-ion concentration is so great that (RH) >> (I^-). If I^- takes up protons to form mainly SH, we measure the velocity of the protolytic reaction between RH and B, that is, the velocity of dissociation of the very weak acid RH. If I^- takes up protons to form mainly RH, the apparent basic catalysis is a disguised acid catalysis of the ion I^-. If neither of the two possibilities is specially favored, we get an apparent basic catalysis which is the result of both a protolytic reaction between RH and the bases and between the acids and I^-. It is impossible to decide from the kinetic experiments under these circum-

stances which of the three possible cases we have in a given reaction. However, we may do this, if we take a solution which is so alkaline that the prototropic substance is completely ionized, suddenly add an excess of strong acid, and examine how much is formed of each of the two isomerides.

If the mechanism in scheme 25 is analyzed mathematically in the same way as scheme 24 an analogous result is obtained. If the hydrogen-ion concentration is so small that the concentration of the ion IH_2^+ is negligible compared with that of RH, the reaction RH $\rightarrow$ SH appears as a unimolecular reaction catalyzed by acids in general. If IH_2^+ by giving up a proton to the base B is predominatingly transformed into SH, we have a genuine acid catalysis of RH. In this case we measure the velocity with which RH receives protons from the acids present. If, on the other hand, the transformation of IH_2^+ into RH is highly favored we have a disguised basic catalysis of IH_2^+, whose concentration is proportional to the hydrogen-ion concentration. We here measure that particular protolytic reaction between IH_2^+ and B by which SH is formed. If neither of the two possibilities is specially favored, we get an apparent acid catalysis which is the result of both protolytic reactions.

The results found here for protolytic reactions with bond-shifting should also hold for those with only proton-shifting mentioned on page 589, but it has not yet been possible to measure the velocity in any such system.

In order to study the mechanism of prototropic isomerization in more detail we must consider the question by which of the reactions 20 to 23 the bond-shifting takes place. We denote by one dash the bond configuration of HX·Y:Z, and by two dashes that of X:Y·ZH. Hence we may write the tautomeric equilibria 20 to 23 in the following way

$$RH' \rightleftarrows RH'', \qquad SH' \rightleftarrows SH'', \qquad I^{-\prime} \rightleftarrows I^{-\prime\prime} \qquad \text{and } IH_2^{+\prime} \rightleftarrows IH_2^{+\prime\prime}$$

The total isomerization RH′ $\rightarrow$ SH″ may take place in the ways contained in the following scheme, where we have left out the acids and bases which take part in the protolytic reactions.

$$\begin{array}{ccccccc} IH_2^{+\prime} & \rightleftarrows & RH' & \rightleftarrows & I^{-\prime} & \rightleftarrows & SH' \\ \downarrow\uparrow(23) & & \downarrow\uparrow(20) & & \downarrow\uparrow(22) & & \downarrow\uparrow(21) \\ IH_2^{+\prime\prime} & \rightleftarrows & RH'' & \rightleftarrows & I^{-\prime\prime} & \rightleftarrows & SH'' \end{array} \tag{29}$$

One of the tautomeric forms of the equilibria 20 to 23 may often be present only in very small quantity compared with the other. Thus the equilibria 20 and 21 will for electrostatic reasons always be highly displaced in favor of the uncharged forms RH′ and SH″. It is often possible to predict from the constitution which of the tautomers of equilibria 22 and 23

is predominating. Thus in the case of acetone the concentration of $I^{-\prime}$ ($\bar{C}H_2 \cdot CO \cdot CH_3$) will probably be very small compared with that of $I^{-\prime\prime}$ ($CH_2{:}C\bar{O} \cdot CH_3$).

Strictly, we cannot speak in the ordinary sense of concentration of the single tautomerides. However, in a given reaction a certain fraction will behave as if it had one constitution, the rest as if it had the other. If we ascribe to the single members of the above tautomeric equilibria a definite concentration, this therefore implies the assumption that the same fraction of a given tautomeric substance behaves as if it had one of the constitutions in all protolytic reactions concerned.

One or more of the reactions in scheme 29 may be excluded for structural reasons. If the atom X in the original molecule $HX \cdot Y{:}Z$ has a complete octet of shared electrons, a bond-shifting can take place only after X has given off a proton. This is the case when X is a carbon atom. Thus, when RH′ is the keto form of acetone, the reactions 20 and 23 are excluded. It has been found by Dawson (17) that the enolization of acetone is catalyzed by both acids and bases. The only possible mechanism for the acid catalysis is that expressed by the scheme

$$\underset{(RH')}{CH_3 \cdot CO \cdot CH_3} \rightleftarrows \underset{(IH_2^{+\prime})}{CH_3 \cdot (C{:}\overset{+}{O}H) \cdot CH_3} \rightleftarrows \underset{(SH')}{\bar{C}H_2 \cdot (C{:}\overset{+}{O}H) \cdot CH_3} \rightleftarrows \underset{(SH'')}{CH_2{:}COH \cdot CH_3}$$

There can be no doubt that the ion $CH_3 \cdot (C{:}\overset{+}{O}H).CH_3$ will give off a proton bound to the oxygen atom much more easily than one bound to a carbon atom. Consequently, the reaction denoted by a heavy arrow in the scheme determines the velocity of the prototropic isomerization. Here the apparent acid catalysis is a basic catalysis of the ion $CH_3 \cdot (C{:}\overset{+}{O}H) \cdot CH_3$. If it were possible to follow the opposite reaction, the ketonization of the enol form of acetone, we would also find general acid catalysis. In this case we would have a genuine acid catalysis of the form $\bar{C}H_2 \cdot (C{:}\overset{+}{O}H) \cdot CH_3$, which is, however, present only in extremely small concentration.

If both X and Z in the original molecule have complete octets of shared electrons, the only way of bond-shifting is by reaction 22 in scheme 29. Thus the prototropic isomerization of a pure three-carbon system (that is a system where the only possible prototropy is of the type $C \cdot C{:}C \rightleftarrows C{:}C \cdot C$) proceeds in the following way

$$RH' \rightleftarrows I^{-\prime} \rightleftarrows I^{-\prime\prime} \rightleftarrows SH'' \tag{31}$$

According to this mechanism the reaction is catalyzed by bases, but not by acids. As far as known, acid catalysis has never been found in such sys-

tems. However, it has been found in some three-carbon systems of the type O:C·C:C·C ⇄ O:C·C·C:C, e.g., glutaconic acid (18). Here it may be explained as a basic catalysis of the ion $\overset{+}{H}O$:C·C:C·C.

The mechanism expressed in scheme 31 seems to be very common in prototropic reactions. It is the only one which we can never exclude. It is of interest to examine it a little further in order to find which of the single reactions determines the velocity of isomerization. The ordinary (apparent) acid strength of the prototropic system

$$K = (H^+)\frac{(I^{-\prime}) + (I^{-\prime\prime})}{(RH) + (SH)}$$

is no measure of the real strengths of the acids RH and SH. These may formally be defined by the equations

$$K_{RH} = (H^+)\frac{(I^{-\prime})}{(RH)} \quad \text{and} \quad K_{SH} = (H^+)\frac{(I^{-\prime\prime})}{(SH)}$$

where it is assumed that equilibrium 31 is attained. The apparent strength is between the real strengths of the two acids. If the fraction ϵ of the prototropic system is of the form SH when equilibrium is attained, we have

$$\frac{K_{RH}}{K_{SH}} = \frac{(I^{-\prime})(SH)}{(I^{-\prime\prime})(RH)} = \frac{\epsilon}{1-\epsilon}\frac{(I^{-\prime})}{(I^{-\prime\prime})} \tag{32}$$

If the medium contains an acid A the reactions $I^{-\prime} + A \rightarrow RH' + B$ and $I^{-\prime\prime} + A \rightarrow SH'' + B$ will take place with velocities which we denote by v' and v'' respectively. v' and v'' depend upon the concentrations and basic strengths of $I^{-\prime}$ and $I^{-\prime\prime}$. By means of formulas 8 and 32 we get the following approximate expression for the ratio of the velocities

$$\frac{v'}{v''} = \frac{(I^{-\prime})}{(I^{-\prime\prime})}\left(\frac{K_{SH}}{K_{RH}}\right)^{\beta} = \frac{1-\epsilon}{\epsilon}\left(\frac{K_{RH}}{K_{SH}}\right)^{1-\beta}$$

From this equation we get the following rules. When SH is a very much stronger acid than RH and ϵ is not extremely small, we have $v'' >> v'$, that is, the velocity of the prototropic reaction is determined by the protolytic reaction between RH and the bases. If, on the other hand RH is very much stronger than SH and $1-\epsilon$ not extremely small, we have $v' >> v''$, that is, the velocity of the prototropic reaction is determined by the protolytic reaction between $I^{-\prime\prime}$ and the acids.

As an example we shall discuss the basic catalysis of the enolization of acetoacetic ester $CH_3COCH_2COOC_2H_5$ (35, 36). For simplicity we only

write $O{:}C{\cdot}CH_2$. From scheme 29 we find the following two possible mechanisms

$$\underset{(RH')}{O{:}C{\cdot}CH_2} \rightleftarrows \underset{(I^{-\prime})}{O{:}C{\cdot}CH} \rightleftarrows \underset{(I^{-\prime\prime})}{O{\cdot}C{:}CH} \rightleftarrows \underset{(SH'')}{HO{\cdot}C{:}CH} \tag{33}$$

and

$$\underset{(RH')}{O{:}C{\cdot}CH_2} \rightleftarrows \underset{(I^{-\prime})}{O{:}C{\cdot}\overset{-}{C}H} \rightleftarrows \underset{(SH')}{H\overset{+}{O}{:}C{\cdot}\overset{-}{C}H} \rightleftarrows \underset{(SH'')}{HO{\cdot}C{:}CH} \tag{34}$$

The acid strength of the enol form SH″ is undoubtedly so much greater than that of the keto form RH′ that, although ϵ is only 0.004, the ion I^- will mainly form SH″ when it reacts with acids. Consequently the reaction denoted by a heavy arrow determines the velocity of the total process 33. However, when we consider scheme 34, the ion $I^{-\prime}$ will undoubtedly take up protons much more quickly at the carbon atom than at the oxygen atom. In other words, the reaction $I^{-\prime} \rightarrow SH'$ will be much slower than $RH' \rightarrow I^{-\prime}$. From this we conclude that the mechanism in scheme 34 is of no importance for the isomerization. This proceeds by reaction 33. We measure the velocity of dissociation of the extremely weak acid, the keto form of acetoacetic ester. If we measured the opposite reaction, the ketonization of the enol form, we would also find general basic catalysis, but this would in reality be a reaction between the ion $I^{-\prime}$ and the acids: $I^{-\prime} + A \rightarrow RH' + B$.

The basic catalysis of the enolization of acetone follows probably the same mechanism, but here the conclusions are less safe, because ϵ is so small that it has been impossible to measure it.

Protolytic reactions between ordinary acids or bases are generally too rapid to be measured. When the acid or base is so weak that we might expect to find a slow reaction, it is generally impossible to measure the rate because equilibrium is attained when too little of the corresponding system is formed. The reason why it is sometimes possible to measure the velocity of protolytic reactions in prototropic systems is to be sought in the tautomerisms 20 to 23. The rate of the protolytic reaction of one of the acids (or bases) in scheme 29 is measurable if the acid (or base) is sufficiently weak and its corresponding base (or acid) is transformed sufficiently completely into its tautomer. It may be measurable even when the acid (or base) is not especially weak, if the concentration of the acid (or base) is kept sufficiently small by a tautomerism. Examples of these two types of protolytic reactions may be found in the discussion of acid catalysis of the isomerization of acetone (scheme 30).

We may add a few words on the pseudo acids. The usual idea of the mechanism of dissociation (Hantzsch (19)) is expressed by the scheme

$$RH \rightleftarrows SH \rightleftarrows S^- + H^+ \tag{35}$$

RH is called a pseudo acid, and SH the aci-form. This opinion is not supported by the points of view maintained in this paper. The system RH ⇄ SH is an ordinary prototropic system. The mechanism of neutralization follows not scheme 35 but 31. There is no difference in principle between the acid character of the pseudo and aci-form. They are both genuine acids, but the pseudo form is a much weaker acid than the aci-form (cf. the discussion of scheme 31). The so-called pseudo acids are not false acids, but acids with false strength.

SUMMARY

Brönsted's theory of acid and basic catalysis and our knowledge of protolytic reactions have been discussed.

Experiments on the decomposition of nitramide have been compared with the theory.

Some of the main results in the study of prototropic reactions have been pointed out.

Lowry's electrolytic theory of prototropic reactions has been criticized.

Another mechanism of prototropic reactions has been discussed.

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THE VELOCITY OF BROMINATION OF ACETOACETIC ETHYL ESTER. II

The General Basic Catalysis

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In Part I (10) the bromination of acetoacetic ethyl ester was studied in pure water and solutions of hydrochloric acid. It was found that the reaction may be expressed by the schemes 1a–1d (Part I, p. 751). Thus four consecutive reactions could be distinguished: (a) the acetoacetic ester is enolized, and (b) brominated to the keto form of α-monobromo-acetoacetic ester; (c) this is enolized, and (d) brominated to α,α-dibromo-acetoacetic ester. Only reactions 1a and 1c take place with measurable velocity. Hydrogen ions do not catalyze to any perceptible degree.

In this part of the investigation the bromination of acetoacetic ethyl ester is studied in buffer solutions containing a weak acid (HB) and its sodium salt (NaB), or, if we use Brönsted's definition (3) of acids and bases, an acid (HB) and its corresponding base (B^-). The hydrogen-ion concentration was as a rule greater than 10^{-5}. The measurements agree with the mechanism expressed in the schemes 1a–1d when we assume that the enolizations of acetoacetic ester and α-mono-bromoacetoacetic ester are catalyzed by the base B^-.

We use the following symbols in addition to those given in Part I, p. 752.[1]

k_B and h_B, catalytic constants for the catalysis by B^- of the enolization of acetoacetic ester (HR) and α-monobromoacetoacetic ester (HR′), respectively.

a, stoichiometrical initial concentration of the acid HB.

b, stoichiometrical initial concentration of the salt NaB.

It will be shown that the velocity of bromination can be explained by assuming that it is determined by two consecutive reactions with the velocities $[k_0 + k_B (B)^-]$ (HR) and $[h_0 + h_B(B^-)]$ (HR′). Owing to the

[1] In Part I, page 759, line 6, the following misprint occurs:

$$\frac{\sqrt{\Sigma\delta^2}}{n-1} \text{ should read } \sqrt{\frac{\Sigma\delta^2}{n-1}}$$

hydrobromic acid formed by the bromination, the concentration of the catalyst will decrease during the reaction.

From these assumptions we shall first deduce a mathematical expression for the course of the reaction. Then we shall show that the expression agrees with the experiments.

When the subscripts 0 and ∞ denote that the concentration corresponds with $t = 0$ and $t = \infty$, respectively, we have for the concentration of the catalyst

$$(B^-)_0 = b + (H^+)_0, \qquad (B^-) = b + (H^+) - \frac{x}{2}$$

and

$$(B^-)_\infty = b + (H^+)_\infty - 2c \tag{19}$$

(H^+) varies so little during reaction that it is sufficient to assume that its increase is proportional to x. From a rough value of the dissociation constant K_{HB} we calculate $(H^+)_0$ and the hydrogen-ion concentration $(H^+)_m$ corresponding to $\frac{x}{2} = c$. We calculate the proportionality factor κ from the equation

$$(H^+)_m - (H^+)_0 = \kappa \frac{c}{2}$$

We then have

$$(H^+) = (H^+)_0 + \kappa \frac{x}{2}$$

which we introduce into equation 19:

$$(B^-)_0 = b + (H^+)_0 \qquad (B^-) = (B^-)_0 - (2 - \kappa)\frac{x}{4}$$

and

$$(B^-)_\infty = (B^-)_0 - (2 - \kappa)c \tag{20}$$

In some cases the increase in (H^+) is so small that we can disregard it and put $\kappa = 0$.

The course of the reaction is determined by the differential equations

$$-\frac{d(HR)}{dt} = [k_0 + k_B(B^-)](HR) \tag{21}$$

and

$$\frac{d(HR')}{dt} = [k_0 + k_B(B^-)](HR) - [h_0 + h_B(B^-)](HR') \tag{22}$$

While the expressions in square brackets are not constant we may with good approximation consider the ratio

$$r = \frac{h_0 + h_B(B^-)}{k_0 + k_B(B^-)} \tag{23}$$

as constant. Provided that one of the following conditions holds, r is a constant:

$$(1)\ \frac{h_0}{k_0} = \frac{h_B}{k_B}$$

$$(2)\ h_0 << h_B(B^-) \text{ and } k_0 << k_B(B^-)$$

and

$$(3)\ b >> \frac{x}{2}\ .$$

They all hold approximately.

From the equations 21, 22, and 23 we get

$$\frac{d(HR')}{d(HR)} = r\frac{(HR')}{(HR)} - 1$$

which is identical with expression 9 in Part I, p. 753. By integration we get expression 10. When $r > 1$, equation 10 approaches the following equation as t increases

$$\frac{(HR')}{(HR)} = \frac{1}{r-1}$$

By introducing this into equation 4, we get

$$c - \frac{x}{4} = (HR)\left(1 + \frac{1}{2(r-1)}\right) \tag{24}$$

If r is sufficiently great, equation 24 will only fail for very small values of t. If we eliminate (HR) from equation 21 and 24 we get

$$\frac{1}{4}\frac{dx}{dt} = k_B\left[(B^-) + \frac{k_0}{k_B}\right]\left(c - \frac{x}{4}\right)$$

By introducing (B^-) from equation 20 we get

$$\frac{1}{4}\frac{dx}{dt} = k_B\left[(B^-)_0 + \frac{k_0}{k_B} - (2-\kappa)\frac{x}{4}\right]\left(c - \frac{x}{4}\right)$$

If we integrate and use equation 20 we obtain

$$k^*t = f(x) + \log_{10} S \tag{25}$$

where we have used the abbreviations

$$k \equiv k_0 + k_B(B^-)_\infty \tag{26}$$

and

$$f(x) \equiv \log_{10} \frac{(B^-) + \dfrac{k_0}{k_B}}{(B^-)_0 + \dfrac{k_0}{k_B}} - \log_{10} \frac{c - \dfrac{x}{4}}{c} \tag{27}$$

and S is an integration constant.

In order to test the agreement between expression 25 and the experiments, we introduce the observed values of x into $f(x)$. (B^-) is calculated from x by means of equation 20. For a first approximation we may use $k_0/k_B = 0$ or a preliminarily estimated value. We now plot $f(x)$ against t. When t is sufficiently great the points fall on a straight line, whose slope determines a preliminary value of k^*. From expression 26 we find the corresponding value of $k_B{}^*$ and of k_0/k_B. We repeat the computation with the new value of k_0/k_B and continue in the same way until a new repetition does not alter the value of k^*. The intercept on the ordinate axis of the straight line is $-\log S$.

Equation 25 does not hold for the observed values of x during the first part of the experiment. Owing to mathematical difficulties we must refrain from testing the explanation for this part of the reaction. If instead of using the observed values of x we use those determined by means of equation 24, equation 25 will hold for the whole experiment. When $t = 0$, we have $(HR) = c\,(1-\epsilon)$, and, consequently, by equation 24 when we use the abbreviation 12

$$c - \frac{x}{4} = c(1-\epsilon)\left(1 + \frac{1}{2(r-1)}\right) = Ac$$

If we introduce this expression together with $t = 0$ into equation 25 we get

$$\frac{A-1}{A} = \frac{S-1}{S} \frac{(B^-)_0 + \dfrac{k_0}{k_B}}{(B^-)_\infty + \dfrac{k_0}{k_B}} \tag{28}$$

By means of this expression we calculate A from S, determined from the experiment as mentioned above. From A we find r, and, by introducing this and the known values of $k_0{}^*$, $h_0{}^*$, and $k_B{}^*$ into equation 23, we find $h_B{}^*$.

Owing to the approximate character of the calculations we can not ex-

pect to get a great accuracy in the determination of the catalytic constant, especially in the case of h_B*.

THE HYDROLYSIS OF BROMINE

In an aqueous solution of bromine we have the following equilibria

$$Br_2 + H_2O \rightleftarrows HBrO + H^+ + Br^- \tag{29}$$

and

$$Br_2 + Br^- \rightleftarrows Br_3^- \tag{30}$$

We neglect a possible formation of the ion Br_5^-. The hydrobromic acid formed by scheme 29 will cause a decrease in the concentration of the catalyst. In order to repress the hydrolysis all experiments were done in 0.05 *M* potassium bromide. We shall here see that this is sufficient to make the error negligible.

The equilibrium constants of the reactions in scheme 29 determined by Bray and Connolly (2) and in scheme 30 determined by Jakowkin (7) are

$$(H^+)(Br^-)(HBrO)/(Br_2) = 5.2 \times 10^{-9}$$

and

$$(Br^-)(Br_2)/(Br_3^-) = 0.063$$

The normality of the bromine is $d = 2(Br_2) + 2(Br_3^-)$. We get

$$(HBrO) = \frac{1.6 \times 10^{-10} d}{(0.063 + (Br^-))(H^+)(Br^-)}$$

In the experiments (Br^-) was 0.05, d usually about 0.02, and $(H^+) > 10^{-5}$. For these values we get $(HBrO) < 6 \times 10^{-5}$. The hydrobromic acid formed by the hydrolysis is equivalent to the (HBrO). When $b > 0.01$ the formation of 6×10^{-5} *N* strong acid is without importance.

EXPERIMENTAL

The bromination of acetoacetic ester was examined in the following five solutions: (1) acetic acid + sodium acetate; (2) glycolic acid + sodium glycolate; (3) chloroacetic acid + sodium chloroacetate; (4) phosphoric acid + primary potassium phosphate; (5) acid sodium sulfate + normal sodium sulfate.

Kahlbaum's acetic acid "for analysis" was used without purification. Glycolic acid was purified as described in reference 9. Chloroacetic acid (pure, "Merck") was distilled. The buffer solutions were made by adding sodium hydroxide to solutions of the acids. The phosphate mixtures were made from Kahlbaum's primary potassium phosphate (for Sörensen's buffer solutions) and hydrochloric acid. The sulfate mixtures were made

from sulfuric acid and sodium hydroxide. The hydrogen-ion concentration was always so great that it was unnecessary to keep the solutions carbon dioxide-free. Sufficient potassium bromide solution was added to make the solutions 0.05 M with respect to this substance during the bromination. The initial concentration of bromine was always about 0.02 N, except in experiments carried out in order to show that the concentration of bromine has no influence on the velocity. The volume of the reacting solution was always 200 cc. The experimental procedure was the same as described in Part I.

In computing the catalytic constants k_B^* and h_B^* we have used the values of ϵ, k_0^*, and h_0^* found for the water reaction (the "uncatalyzed" reaction) in 0.05 M potassium bromide by the experiments given in table 4 (Part I, p. 761). Other salts present in the catalytic experiments may also have an effect on the water reaction. It has already been shown that the kinetic salt effect of sodium chloride on k_0^* and h_0^* is small, and the effects of the other salts are probably also small. Since, further, the water reaction usually plays a rather insignificant part compared with the catalytic reaction, we have always neglected a possible salt effect on k_0^* and h_0^* in the calculation of k_B^* and h_B^*. The error thus committed is probably insignificant, except in the experiments in sulfate mixtures. Here the salt effect on the water reaction is probably greater than in the other experiments, and it has an especially great influence on the value of the catalytic constant, because the sulfate ion catalysis is only a small part of the total reaction.

Acetate ion catalysis

It was first shown that even a great variation in the concentration of bromine did not affect the velocity of bromination in the acetate buffers. This is seen especially clearly from four series of preliminary experiments in acetate buffers (8). Here an insufficient amount of bromine was added and the moment when the reaction ceased because all bromine had reacted was determined electrometrically by means of the arrangement described in Part I, p. 757. The mean value of k_B^* found here was 7.47 (at 18°C.), while $k_B^* = 7.41$ was found by the experiments with an excess of bromine in this paper.

The velocity is independent of the concentration of undissociated acetic acid (table 1) and thus also independent of the hydrogen- and hydroxyl-ion concentration of the acetate buffer, when the acetate ion concentration is kept constant.

Table 4 gives a summary of ten series of experiments in different mixtures of acetic acid and sodium acetate at the temperatures 0.03, 17.94, and 24.97°C. The results of two of the series are given in more detail in tables 2 and 3.

The constant k^* has been computed by plotting $f(x)$ against t as described above. In the last column of tables 2 and 3 $\delta = f(x) - (k^* t - \log S)$ has been tabulated. The agreement with formula 25 is always good when $0.8 > (c - \frac{x}{4})/c > 0.5$. In the first part of the reaction, when $(c - \frac{x}{4})/c > 0.8$, too great values of $f(x)$ are obtained. This is in qualitative agreement with the theory, but owing to mathematical difficulties we cannot test the agreement quantitatively. Later in the reaction, when $(c - \frac{x}{4})/c < 0.5$, we get greater and greater discrepancies, corresponding to too small values of x. This was also found in experiments in pure water and hydrochloric acid and is probably due to a secondary reaction. In this period of the reaction the solution acquired a peculiar sharp smell and, toward the end of the reaction, it turned cloudy.

TABLE 1

Bromination of acetoacetic ester in acetic acid–sodium acetate mixtures at 18°C.

	b = 0 04008			b = 0 02004	
	a = 0 110	a = 0 060		a = 0 080	a = 0 030
t	$(c - \frac{x}{4})/c$	$(c - \frac{x}{4})/c$	t	$(c - \frac{x}{4})/c$	$(c - \frac{x}{4})/c$
0 250	0 8584	0 8584	1 500	0 6001	0 6009
0 495	0 7246	0 7246	3 000	0 3674	0 3725
1.005	0 5114	0 5117			

TABLE 2

Bromination of acetoacetic ester in a mixture of acetic acid and sodium acetate at 0.03°C.
$a = 0.0600$; $b = 0.04008$; $c = 5.291 \times 10^{-3}$; (KBr) = 0.050; $K_{HB} = 3 \times 10^{-5}$; $(B^-) = 0.04013 - \frac{x}{2}$; $(B^-)_\infty = 0.02955$; $k^* = 0.05144$; $\log S = 0.0113$; $k_B = 1.621$; $h_B^* = 23$

t	$\frac{x}{4} \times 10^3$	$f(x)$	$k^*t - \log S$	$\delta \times 10^4$
1.003	0.633	0.0421	0 0403	+18
1.997	1 261	0.0915	0.0914	+1
2.497	1.553	0.1177	0.1171	+6
2.997	1.808	0.1426	0.1429	−3
3.497	2 052	0.1688	0.1686	+2
4.000	2.275	0.1947	0.1945	+2
4.502	2.419	0.2199	0.2203	−4
5.003	2.667	0.2460	0.2461	−1
5.997	2.998	0.2950	0 2972	−22

From the summary of all the experiments in acetate mixtures given in table 4 it is seen that the constancy of $k_B{}^*$ at constant temperature is good even when the acetate concentration is varied considerably. The mutual

TABLE 3

Bromination of acetoacetic ester in a mixture of acetic acid and sodium acetate at 17.94°C.

$a = 0.0900$; $b = 0.06012$; $c = 6.275 \times 10^{-3}$; (KBr) = 0.050; $K_{HB} = 3 \times 10^{-5}$; $(B^-) = 0.06017 - \frac{x}{2}$; $(B^-)_\infty = 0.04762$; $k^* = 0.3718$; $\log S = 0.0099$; $k_B{}^* = 7.43$; $h_B{}^* = 121$

t	$\frac{x}{4} \times 10^3$	$f(x)$	$k^*t - \log S$	$\delta \times 10^4$
0.103	0.514	0 0299	0 0284	+15
0.200	1.049	0.0646	0.0645	+1
0.300	1.552	0.1014	0.1016	−2
0.398	2.003	0.1383	0 1381	+2
0.500	2.411	0.1758	0.1760	−2
0.595	2.759	0.2115	0 2113	+2
0.700	3.084	0 2486	0 2504	−18

TABLE 4

Bromination of acetoacetic ester in mixtures of acetic acid and sodium acetate at 0, 18, and 25°C.

(KBr) = 0.050 in all experiments

TEMPERATURE	$(B^-)_0$	$(B^-)_\infty$	k^*	$k_B{}^*$	$h_B{}^*$	MEAN VALUES $k_B{}^*$	MEAN VALUES $h_B{}^*$
degrees C.							
0.03	0.04013	0.02955	0 05144	1.621	23	1.620	25
	0.1002	0.08967	0.1488	1.620	27		
17.94	0.02009	0.01381	0.1208	7.46	98	7.41	119
	0.02009	0.00998	0 0912	7.38	121		
	0.04013	0 03385	0.2691	7.42	112		
	0.06017	0.05389	0.4162	7.39	127		
	0.06017	0.04762	0.3718	7.43	121		
	0.08021	0 07393	0.5645	7.39	137		
24 97	0.02009	0.01513	0.2222	12.62	214	12.70	210
	0.04013	0 03020	0 4170	12 77	207		

agreement of the values of $h_B{}^*$ is not very good. However, when we remember that we can only obtain a rough value of this constant, we might not expect a better agreement.

Glycolate ion catalysis

Table 5 gives the results of a single series of experiments, and table 6 a summary of all the experiments in mixtures of glycolic acid and sodium

TABLE 5

Bromination of acetoacetic ester in a mixture of glycolic acid and sodium glycolate at 0.03°C.

$a = 0.0136$; $b = 0.05550$; $c = 3.056 \times 10^{-3}$; (KBr) = 0.050; $k_{HB} = 2.2 \times 10^4$; $(B^-) = 0.05555 - 1.99 \times \frac{x}{4}$; $(B^-)_\infty = 0.04948$; $k^* = 0.02630$; $\log S = 0.0128$; $k_B^* = 0.460$; $h_B^* = 6.87$

t	$\frac{x}{4} \times 10^3$	$f(x)$	$k^*t - \log S$	$\delta \times 10^4$
3 00	0 474	0.0666	0 0661	+5
5 00	0.788	0 1187	0 1187	0
5 00	0.790	0 1189	0 1187	+2
7 00	1 064	0 1710	0.1713	−3
9 00	1.307	0.2241	0 2239	+2
11.00	1 516	0 2764	0.2765	−1

TABLE 6

Bromination of acetoacetic ester in mixtures of glycolic acid and sodium glycolate at 0, 18, and 25°C.

(KBr) = 0.050 in all experiments

TEMPERATURE	$(B^-)_0$	$(B^-)_\infty$	k^*	k_B^*	h_B^*	MEAN VALUES k_B^*	MEAN VALUES h_B^*
degrees C.							
0 03	0 05555	0 04948	0.02630	0.460	6 87	0 462	6 62
	0.09256	0 08645	0 04357	0 463	6 36		
17.94	0 05555	0.04948	0.1197	2 06	29.4	2 06	28 4
	0 09256	0.08645	0.1958	2 06	27.3		
24 97	0.05555	0.04948	0.2032	3.48	53 6	3 48	53.4
	0.09256	0.08645	0.332	3.48	53.2		

glycolate. The dissociation constant K_{HB} at different salt concentration has been taken from a yet unpublished determination. The agreement of the kinetic experiments with the theory is as good as in the experiments on acetate ion catalysis.

Monochloroacetate ion catalysis

Table 7 gives the results of a single series of experiments, and table 8 a summary of all the experiments in mixtures of monochloroacetic acid and sodium monochloroacetate. The dissociation constant of monochloroace-

TABLE 7

Bromination of acetoacetic ester in a mixture of monochloroacetic acid and sodium monochloroacetate at 17.94°C.

$a = 0.1018$; $b = 0.1002$; $c = 3.382 \times 10^{-3}$; (KBr) = 0.050; $K_{HB} = 0.0023$; $(B^-) = 0.1024 - 1.92 \times \frac{x}{4}$; $(B^-)_\infty = 0.0959$; $k^* = 0.0709$; $\log S = 0.0145$; $k_B = 0.554$; $h_B^* = 7.8$

t	$\frac{x}{4} \times 10^3$	$f(x)$	$k^*t - \log S$	$\delta \times 10^4$
1.000	0.446	0 0586	0 0564	+22
2 000	0.893	0 1276	0.1273	+3
2.500	1.092	0 1626	0.1627	−1
3.000	1.274	0 1974	0.1982	−8
3.500	1.447	0 2335	0 2337	−2
4 000	1 601	0 2685	0 2691	−6
5 000	1.880	0 3408	0.3400	+8
6.000	2 098	0 4046	0.4109	−63

TABLE 8

Bromination of acetoacetic ester in mixtures of monochloroacetic acid and sodium monochloroacetate at 0, 18, and 25°C.

(KBr) = 0.050 in all experiments

TEMPERATURE	$(B^-)_0$	$(B^-)_\infty$	k^*	k_B^*	h_B^*	MEAN VALUES	
						k_B^*	h_B^*
degrees C.							
0.03	0 06226	0 05597	0 01001	0.1158	1.71	0.1162	1.62
	0.1024	0 0959	0.01470	0 1165	1.54		
17.94	0 06226	0 05597	0.0488	0.554	8 0	0.554	7.9
	0.1024	0 0959	0 0709	0.554	7 8		
24.97	0.04218	0 03611	0.0669	0.989	11.6	0.983	12.0
	0.1024	0 0959	0.1250	0.978	12.3		

tic acid at 20°C. and in infinite dilution $K_{HB}^0 = 1.41 \times 10^{-3}$ has been determined by Grove (6). From this value and the assumption that the relative increase of K_{HB} by addition of salt is the same as for glycolic acid, it is estimated that the value $K_{HB} = 2.3 \times 10^{-3}$ is sufficiently accurate

for calculation of (H^+) in all the experiments. Also here the agreement is good.

Primary phosphate ion catalysis

Table 9 gives the results of a single series of experiments, and table 10 a summary of all the experiments in mixtures of phosphoric acid and primary potassium phosphate. The values of the first dissociation constant of phosphoric acid used for the calculation of (H^+) have been calculated from the measurements of Bjerrum and Unmack (1) at 18°C. and 25°C. These measurements have been carried out in solutions containing sodium

TABLE 9

Bromination of acetoacetic ester in a mixture of phosphoric acid and primary potassium phosphate at 24.97°C.

$a = 0.01520$; $b = 0.06085$; $c = 3.056 \times 10^{-3}$; (KBr) = 0.050; (KCl) = 0.015; $K_{HB} = 0.0089$; $(B^-) = 0.06274 - 1.69 \times \frac{x}{4}$; $(B^-)_\infty = 0.05758$; $k^* = 0.0817$; $\log S = 0.0160$; $k_B^* = 0.877$; $h_B^* = 10\ 6$

t	$\frac{x}{4} \times 10^3$	$f(x)$	$k^*t - \log S$	$\delta \times 10^4$
1.253	0 0575	0 0863	0 0864	−1
2 000	0 0914	0 1475	0 1474	+1
2.752	0 1206	0 2089	0 2088	+1
3 500	0 1456	0 2701	0 2700	+1
4 253	0 1672	0 3314	0 3315	−1

TABLE 10

Bromination of acetoacetic ester in mixtures of phosphoric acid and primary potassium phosphate at 0, 18, and 25°C.

(KBr) = 0.050 in all experiments

TEMPERATURE	$(B^-)_0$	$(B^-)_\infty$	TOTAL SALT CONCENTRATION s	k^*	k_B^*	h_B^*	MEAN VALUES k_B^*	MEAN VALUES h_B^*
degrees C								
0 03	0 06311	0 05807	0.126	0 00907	0 0954	0.88		
17 94	0 03596	0.03122	0 094	0 03320	0 493	5.9	0.488	5.6
	0.04716	0 04214	0 114	0.03882	0.499	5.6		
	0 07003	0.06468	0.145	0 0491	0 484	5 6		
	0 09259	0.08705	0.170	0.05944	0 478	5 4		
24.97	0 06274	0 05758	0.126	0.0817	0 877	10.6	0.876	11.2
	0.05641	0 05143	0.125	0.07616	0 874	11.7		

ions instead of potassium ions and at salt concentrations $\leqq 0.1\ N$, while the solutions for the catalytic experiments were usually somewhat more concentrated. Nevertheless, the values obtained from the interpolation formulas given by Bjerrum and Unmack are considered to be accurate enough for the rather rough calculation of (H^+). For the experiments at 0°C. the values of $-\log K_{HB}$ at 25°C. and 18°C. have been extrapolated to 0°C. It is assumed that the concentration of the secondary phosphate ion is always negligible.

Formula 25 holds well within the single series of experiments. The part of the total reaction which is caused by the catalysis is only one to two times as great as the part caused by the water reaction. Nevertheless, the constancy of $k_B{}^*$ when the concentration of primary phosphate ion is varied is good. Naturally, the accuracy of $h_B{}^*$ is much smaller, but also here the constancy is fairly good.

The second dissociation constant of sulfuric acid

For the calculation of the experiments on the bromination of acetoacetic ester in mixtures of acid and normal sodium sulfate it is necessary to have some knowledge of the second dissociation constant of sulfuric acid at different salt concentrations. Sherrill and Noyes (13) have calculated this constant K at 25°C. from measurements of the electric conductivity of solutions of sulfuric acid and of acid sodium sulfate. By extrapolation to infinite dilution they find the activity dissociation constant $K^0 = 0.0115$.

Here we shall compute K^0 from their determinations of K in a slightly different way. According to the theory of Debye and Hückel the activity coefficient f_i of an ion in dilute solution may be expressed by the formula

$$-\log f_i = z^2\alpha\sqrt{\mu} - \beta_i\mu$$

where z is the number of electric charges on the ion, μ the ionic strength of the solution, α is a constant, the same for all ions (at 25°C. in water $\alpha = 0.504$), and β_i approaches a constant value, when $\mu \rightarrow 0$. By means of this formula we may express the second dissociation constant of sulfuric acid as follows

$$-\log K = -\log K^0 - 2.016\sqrt{\mu} + \beta\mu$$

We now plot $-\log K + 2.016\sqrt{\mu}$, calculated from the values of Sherrill and Noyes, against μ. The points fall on a straight line which determines the constants $-\log K^0$ and β. We thus find for the solutions of sulfuric acid

$$-\log K = 1.988 - 2.016\sqrt{\mu} + 0.62\mu \qquad (\mu \leqq 0.0844) \qquad (31)$$

and for the solutions of acid sodium sulfate

$$-\log K = 1.984 - 2.016\sqrt{\mu} + 1.27\mu \qquad (\mu \leqq 0.1056) \qquad (32)$$

The agreement is seen from table 11 where the dissociation constants K found by Sherrill and Noyes are given in the third column, while those calculated from the formulas 31 and 32 are given in the last column. By this extrapolation we get $K^0 = 0.0103$ at 25°C.

In order to get an idea of the variation of K^0 with temperature we make the following considerations. Thorvaldson, Brown and Peaker (14) have found calorimetrically that the heat evolved by mixing 1 N H_2SO_4 and an equivalent amount of NaOH, 100 H_2O at 20°C. is 16.984 kg-cal. per equivalent H_2SO_4. Richards and Hall (12) have determined the heats of neutralization of different strong acids and sodium hydroxide. They found for HCl, 100 H_2O + NaOH, 100 H_2O at 20°C. 13.924 kg-cal. and for HBr, HJ, and HNO_3 nearly the same value. Thus sulfuric acid in

TABLE 11

Second dissociation constant of sulfuric acid at 25°C.

SOLUTIONS OF SULFURIC ACID				SOLUTIONS OF ACID SODIUM SULFATE			
$-\log K = 1.988 - 2.016\sqrt{\mu} + 0.62\mu$				$-\log K = 1.984 - 2.016\sqrt{\mu} + 1.27\mu$			
Stoichiometric concentration of H_2SO_4	μ	K (exp.)	K (calcd.)	Stoichiometric concentration of $NaHSO_4$	μ	K (exp.)	K (calcd.)
0.00025	0.0007	0.0118	0.0116	0.000391	0.0011	0.0107	0.0121
0.001	0.0027	0.0130	0.0130	0.000781	0.0022	0.0121	0.0128
0.005	0.0116	0.0168	0.0167	0.001562	0.0044	0.0135	0.0139
0.00625	0.0141	0.0175	0.0175	0.003125	0.0084	0.0153	0.0155
0.0125	0.0225	0.0208	0.0208	0.00625	0.0160	0.0178	0.0178
0.0250	0.0461	0.0260	0.0260	0.0125	0.0302	0.0213	0.0213
0.0500	0.0844	0.0352	0.0352	0.0250	0.0564	0.0265	0.0265
				0.0500	0.1056	0.0348	0.0344

approximately the same molar concentration gives 3 kg-cal. more per equivalent than the strong acids. We may assume that the first dissociation of 1 N H_2SO_4 is practically complete. The difference in the heat of neutralization is probably caused by the second dissociation $HSO_4^- + H_2O \rightarrow SO_4^{--} + H_3O^+$. If the second dissociation constant of sulfuric acid is not many times as great in 1 N H_2SO_4 as by infinite dilution, only few per cent of the acid is present in form of the normal sulfate ion. We thus get from the above measurements that the heat of dissociation of the ion HSO_4^- is approximately 3 kg-cal. per ½ mole or 6 kg-cal. per mole. If we use this value also at infinite dilution and in all the temperature interval 0–25°C. we get from K^0 at 25°C. by means of the formula

$$U = 4.575 \times 10^{-3} \frac{d \log K^0}{d\,(T^{-1})}$$

where U is the heat of dissociation in kilogram-calories per mole per liter and T is the absolute temperature, the following values of K^0:

25°C.	$-\log K^0 = 1.99$	$K^0 = 0.0103$
18°C.	$-\log K^0 = 1.88$	$K^0 = 0.013$
0°C.	$-\log K^0 = 1.58$	$K^0 = 0.026$

Sulfate ion catalysis

Experiments on the bromination of acetoacetic ester were carried out in solutions of sodium sulfate containing a little acid sodium sulfate and 0.050 M potassium bromide ($0.16 < \mu < 0.34$). K was found from equation 32. For experiments at 18°C. and 0°C. the values of $-\log K^0$ found at these

TABLE 12

Bromination of acetoacetic ester in a mixture of acid and normal sodium sulfate at 24.97°C.

$a = 0.00035$; $b = 0.07644$; $c = 3.039 \times 10^{-3}$; (KBr) = 0.050; $K_{HB} = 0.053$; $(B^-) = 0.07658 - 1.16 \times \frac{x}{4}$; $(B^-)_\infty = 0.07306$; $k^* = 0.03785$; $\log S = 0.0164$; $k_B^* = 0.091$; $h_B^* = 1.2$

t	$\frac{x}{4} \times 10^3$	$f(x)$	$k^*t - \log S$	$\delta \times 10^4$
1.00	0.189	0.0277	0.0214	+63
3.00	0.616	0.0976	0 0972	+4
4.00	0.817	0.1350	0 1350	0
5.00	1.002	0.1725	0.1728	−3
6.00	1.175	0.2109	0 2107	+2
7 00	1.330	0.2484	0.2486	−2
8 00	1.475	0.2867	0.2864	+3
9 00	1.603	0.3235	0 3242	−7

temperatures were substituted for 1.984 in equation 32. Owing to the great ionic strength of the solution we can only get very rough values of K in this way. However, we consider the accuracy sufficient for the following reasons. Firstly, the correction for the variation of (H^+) is here very small, and secondly, there is, as we shall see, another source of error which makes it of no use to attempt to determine the concentration of the catalyst with great accuracy.

As seen from table 12 the agreement with formula 25 is as good as in experiments with other catalysts. In table 13 is given a summary of all the experiments in sodium sulfate. It is seen that k^* is only 11 to 24 per cent greater than k_0^*. Thus the velocity is not much increased by the presence of the sodium sulfate. The kinetic salt effect on k_0^* is probably not negligible compared with the increase. However, the increase can not be explained only by the salt effect. We have found in Part I, that 0.1 M

sodium chloride or potassium chloride gives a decrease of the velocity of 1 to 2 per cent. It is therefore most unlikely that the salt effect of 0.1 *M* sodium sulfate can give an increase of 24 per cent. However, the effect of the salt being unknown, it is disregarded. In the other catalytic experiments the error thus introduced is probably of no importance. Here it makes the values of k_B* less reliable. In addition, the experimental error in k* is of greater importance here, where the water reaction is 80 to 90 per cent of the total reaction. In spite of these possible errors, the values of k_B* at different catalyst concentrations agree fairly well among themselves. Naturally, the values of h_B* are only very rough.

We have now examined the bromination of acetoacetic ester in solutions containing one of the following bases,—acetate, glycolate, monochloroace-

TABLE 13

Bromination of acetoacetic ester in mixtures of acid and normal sodium sulfate at 0, 18, and 25°C.

(KBr) = 0.050 in all experiments

TEMPERATURE	$(B^-)_0$	$(B^-)_\infty$	μ	k*	k_B*	h_B*	MEAN VALUES k_B*	MEAN VALUES h_B*
degrees C								
0 03	0 0767	0 0744	0 28	0 004012	0 0065	0 09		
17 94	0.0486	0 0455	0 195	0 02012	0 0510	0 4	0.047	0.5
	0.0766	0 0734	0 28	0.02111	0 0452	0.6		
	0.0961	0.0928	0 34	0 02205	0 0458	0.4		
24 97	0 0383	0.0355	0 16	0 03475	0 100	1 9	0 096	1.5
	0.0766	0.0731	0.28	0 03785	0 091	1.2		

tate, primary phosphate, and sulfate ions—together with the corresponding acid. We have always found agreement with formula 25 for the part of the reaction where a comparison was possible. From this we conclude that the mechanism is as given in scheme 1 (Part I, p. 751), and that the enolization of acetoacetic ester and of α-monobromoacetoacetic ester is catalyzed by bases in general. The theory of general acid and basic catalysis and of prototropic isomerization has recently been discussed in another paper (11), where references to the literature on the subject will be found.

The water reaction studied in part I is explained as the result of the basic catalysis of the water. If we neglect the effect of the association of the water molecules, the concentration of water is $(H_2O) = 55.5$, its basic strength 55.5^{-1} and the catalytic constants $k_{H_2O} = k_0/55.5$ and $h_{H_2O} = h_0/55.5$.

The catalytic constants for the six bases examined are given in table 14

together with the strengths of the acids which correspond to the bases. In the paper (11) mentioned above we have discussed the formula

$$\frac{1}{q} k_B = G\left(\frac{p}{q} K_B^{\circ}\right)^{\beta} \tag{33}$$

where K_B^0 is the strength of the catalyzing base at infinite dilution, p and q are statistical factors, and β and G are constants for a given reaction at a given temperature ($0 < \beta < 1$). In order to test the validity of this

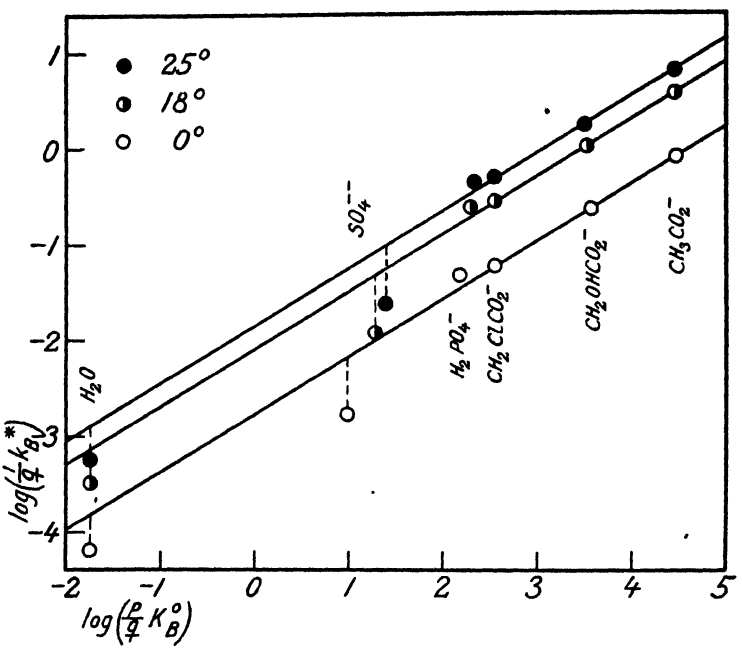


FIG. 1. BASIC CATALYSIS OF THE ENOLIZATION OF ACETOACETIC ESTER
The dependence of catalytic constant upon basic strength

formula for the reaction examined here we plot $\log\left(\frac{1}{q}k_B^*\right)$ and $\log\left(\frac{1}{q}h_B^*\right)$ against $\log\left(\frac{p}{q}K_B^0\right)$ (figure 1 and 2). The points for acetate, glycolate, and monochloroacetate ions fall very close to a straight line. If we draw the line through the points for acetate and glycolate ions we get in the case of acetoacetic ester the following values of β: 0.602, 0.605, and 0.599 at 0, 18, and 25°C., respectively. β is here independent of the temperature. In figure 1 we have drawn all the straight lines with the slope $\beta = 0.60$. This value has also been used for the calculation of G^* from formula 33 (see table 14). For α-monobromoacetoacetic ester, where the accuracy is

much smaller, we get from the catalytic constants of acetate and glycolate ions $\beta = 0.64$, 0.68, and 0.63 at 0, 18, and 25°C., respectively. We have used the value $\beta = 0.64$ for drawing the straight lines in figure 2 and for calculating G^* (table 14). While the agreement with formula 33 is always good for the three carboxylate bases, the catalysis of the primary phosphate ion is a little too strong, and that of the sulfate ion much too weak. This latter deviation of the base with two negative charges is qualitatively in agreement with the theory (11). The points for water fall below the lines. However, the deviation is not unreasonably great when

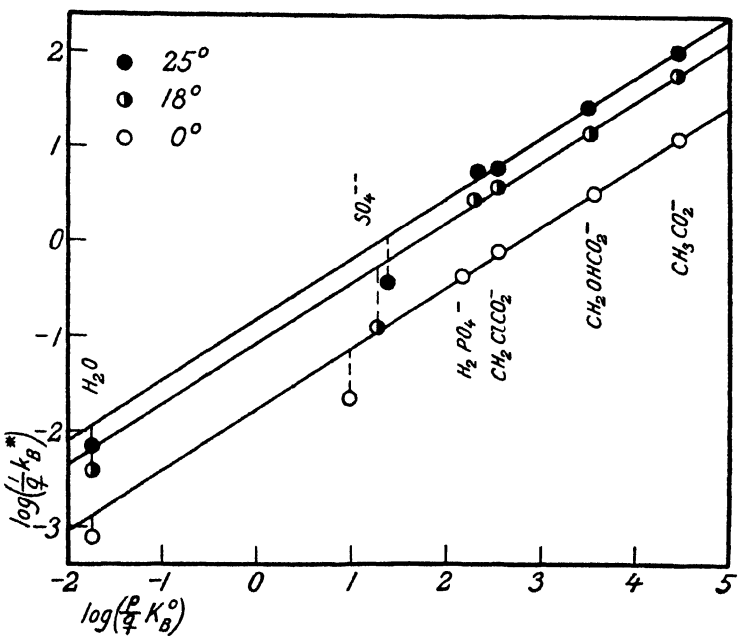


FIG. 2. BASIC CATALYSIS OF THE ENOLIZATION OF α-MONOBROMOACETOACETIC ESTER
The dependence of catalytic constant upon basic strength

we remember that we have neglected the effect of the association. As seen both from the figures and the table, the deviation from formula 33 for a given base is approximately independent of the temperature.

From the experimental values of k_B^* at the three temperatures we get the expressions for $\log k_B^*$ given in table 15. This table also contains the heats of activation Q in kg-cal. calculated from the formula

$$Q = -4.575 \times 10^{-3} \frac{d \log k_B}{d\,(T^{-1})} .$$

The basic strength of a catalyst generally varies with the temperature. The increase in velocity when the temperature rises may therefore formally

TABLE 14

Basic catalysis of the enolization of acetoacetic and α-monobromoacetoacetic ester at 0, 18, and 25°C.

TEMPERATURE	CATALYST					ACETOACETIC ESTER $\beta = 0.60$			α-MONOBROMOACETOACETIC ESTER $\beta = 0.64$		
		p	q	K_{HB}^{0}	$\log\left(\frac{p}{q}K_{B}^{0}\right)$	k_B^*	$\log\left(\frac{1}{q}k_B^*\right)$	$G^* \times 10^3$	k_B^*	$\log\left(\frac{1}{q}k_B^*\right)$	$G^* \times 10$
degrees C.											
0.03	$CH_3CO_2^-$	1	2	1.70×10^{-5} [a]	4.469	1.620	0.908-1	1.69	25	1.097	1.73
	$CH_2OHCO_2^-$	1	2	1.36×10^{-4} [a]	3.566	0.462	0.364-1	1.68	6.62	0.520	1.74
	$CH_2ClCO_2^-$	1	2	1.41×10^{-3} [b]	2.55	0.1162	0.764-2	1.72	1.62	0.909-1	1.90
	$H_2PO_4^-$	3	2	1.00×10^{-2} [d]	2.18	0.0954	0.678-2	2.35	0.88	0.643-1	1.77
	SO_4^{--}	1	4	2.6×10^{-2} [e]	0.98	0.0065	0.211-3	0.42	0.09	0.35-2	0.5
	H_2O	1	1	55.5	−1.74	0.637×10^{-4}	0.804-5	0.70	0.766×10^{-3}	0.884-4	1.00
17.94	$CH_3CO_2^-$	1	2	1.79×10^{-5} [a]	4.447	7.41	0.569	7.96	119	1.775	8.5
	$CH_2OHCO_2^-$	1	2	1.48×10^{-4} [a]	3.528	2.06	0.013	7.87	28.4	1.153	7.9
	$CH_2ClCO_2^-$	1	2	1.41×10^{-3} [b]	2.55	0.554	0.442-1	8.17	7.9	0.597	9.2
	$H_2PO_4^-$	3	2	7.58×10^{-3} [c]	2.296	0.488	0.387-1	10.23	5.6	0.447	9.5
	SO_4^{--}	1	4	1.3×10^{-2} [e]	1.28	0.047	0.073-2	2.02	0.5	0.097-1	1.9
	H_2O	1	1	55.5	−1.74	3.21×10^{-4}	0.506-4	3.55	3.89×10^{-3}	0.590-3	5.0
24.97	$CH_3CO_2^-$	1	2	1.77×10^{-5} [a]	4.450	12.70	0.803	13.6	210	2.021	15.0
	$CH_2OHCO_2^-$	1	2	1.54×10^{-4} [a]	3.511	3.48	0.241	13.6	53.4	1.426	15.2
	$CH_2ClCO_2^-$	1	2	1.41×10^{-3} [b]	2.55	0.983	0.692-1	14.5	12.0	0.779	14.0
	$H_2PO_4^-$	3	2	6.90×10^{-3} [c]	2.337	0.876	0.642-1	17.4	11.2	0.748	18.0
	SO_4^{--}	1	4	1.03×10^{-2} [e]	1.39	0.096	0.380-2	3.52	1.5	0.57-1	4.8
	H_2O	1	1	55.5	−1.74	5.62×10^{-4}	0.750-4	6.22	6.92×10^{-3}	0.840-3	9.0

[a] Unpublished electrometric measurements. [b] At 20°C., Grove (6). [c] Bjerrum and Unmack (1). [d] As (c). Extrapolation to 0°C. [e] This paper, page 614.

be divided in two parts: (1) the increase in velocity at constant basic strength, (2) the change in velocity owing to the change in basic strength. It may be of some interest to consider the first part separately. From formula 33 we find, when we assume that β and K_B^0 are constant, the "heat of activation"

$$Q_G = -4.575 \times 10^{-3} \frac{d \log G}{d (T^{-1})}$$

The values of Q_G calculated from this formula are given in table 15. For monochloroacetic acid we have assumed that the dissociation constant is independent of the temperature. Q_G is approximately constant for all the bases. When we compare bases which have at constant temperature the

TABLE 15

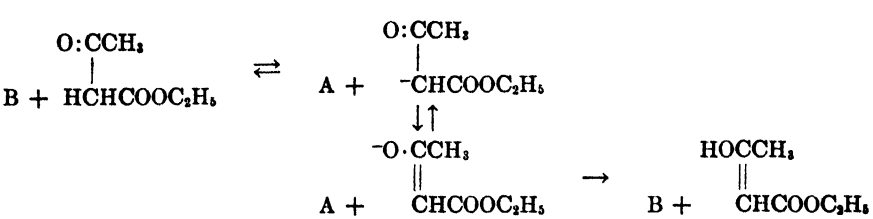
Basic catalysis of the enolization of acetoacetic and α-monobromoacetoacetic ester

The dependence upon temperature; the heat of activation

CATALYST	ACETOACETIC ESTER			α-MONOBROMO-ACETOACETIC ESTER
	$\log k_B^*$ (0°C. – 25°C.)	Q	Q_G	Q
$CH_3CO_2^-$	$10.905 - 2.921 \times 10^3/T$	13.4	13.5	14
$CH_2OHCO_2^-$	$10.166 - 2.868 \times 10^3/T$	13.1	13.6	13.5
$CH_2ClCO_2^-$	$10.125 - 3.021 \times 10^3/T$	13.8	(13.8)	13
$H_2PO_4^-$	$10.487 - 3.143 \times 10^3/T$	14.4	13.0	16
SO_4^{--}	$11.788 - 3.817 \times 10^3/T$	17.5	13.7	
H_2O	$7.130 - 3.093 \times 10^3/T$	14.2	14.2	14

same G^* this must naturally be so. However, Q_G has nearly the same value also for the last three bases, although G^* here varies considerably. It is interesting that the sulfate ion, which has an especially great heat of activation (Q), has the same Q_G as the other bases.

The mechanism of prototropic isomerization was discussed at length in the theoretical paper (11). As shown there the enolization of acetoacetic ester follows the scheme



where the equilibrium between the two forms of the ion is attained practically instantaneously. It follows from the theory that the transference

of protons from the keto-ester to the base determines the velocity of the total reaction, if the tautomeric ion by taking up a proton from an acid forms predominatingly the enol-ester. It was shown that this is probably the case here, because the enol form is a much stronger acid than the keto form. However, we may also test this condition experimentally in the following way.

The apparent dissociation constant of acetoacetic ester at 25°C. is 2.0 $\times 10^{-11}$ (Goldschmidt and Oslan (4)). It is therefore easy to prepare a solution which is so alkaline that the ester is completely ionized. To this solution we suddenly add a mixture containing an excess of hydrochloric acid and bromine water. If only enol is formed this will instantaneously react with bromine (one mole per mole ester). After this the α-monobromoacetoacetic ester formed will react slowly with more bromine. The excess of bromine was removed by adding allyl alcohol immediately after the hydrochloric acid, and the solution was titrated in the ordinary way. It was always found that about one mole of bromine had reacted per mole of ester. However, the experiments were not quite reproducible. When the excess of bromine was small, less than the theoretical amount was used. Similar experiments have been carried out by Grossmann (5). He also finds that acetoacetic ester in sufficiently alkaline solution behaves as if it were exclusively the enol form of the ion. From these considerations we conclude that the velocity of enolization which we have measured in this work is actually the velocity of transference of protons from the keto form to the bases, or, in other words, the velocity of dissociation of the keto form, which is an extremely weak acid.

SUMMARY

This paper contains an experimental study of the rate of bromination of acetoacetic ester in solutions of weak bases and their corresponding acids.

It has been shown that the velocity of bromination is determined by the consecutive enolizations of acetoacetic and α-monobromoacetoacetic ester, which reactions are catalyzed by bases in general.

The catalytic constants of the six bases acetate, glycolate, monochloroacetate, primary phosphate, sulfate ions, and water at 0, 18, and 25°C. have been determined and compared with the strengths of the bases.

Evidence has been given in favor of the view that the velocities of enolization are determined by the velocities of dissociation of the keto forms, which are extremely weak acids.

I wish to thank the head of the laboratory, Professor Niels Bjerrum, for valuable advice and kind interest in my work.

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ADSORPTION OF HYDROGEN BY PALLADIUM BLACK UNDER HIGH PRESSURE

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Among the great number of authors who studied the system "Pd–H_2," many considered the question of the influence of hydrogen pressure upon the adsorptive capacity of palladium, but actual study of the influence of high pressure of hydrogen on its adsorption by palladium occupied the attention of very few investigators. The first work in which high hydrogen pressure was applied to the system "Pd H_2" is the work of Dewar (1), who wanted to clear up the question as to whether a critical temperature exists at which palladium will not adsorb hydrogen at an optional pressure. For this purpose Dewar carried out experiments at temperatures from 360°C. to 600°C. and under hydrogen pressures of 60, 80, and 120 atmospheres.

The results of Dewar's experiments might be summarized in table 1. He found that at 420°C. and 80 atmospheres of hydrogen pressure, the amount of hydrogen adsorbed by palladium is of a magnitude of the order of 225–200 mg. per 100 grams of palladium. Mond, Ramsay, and Shields (6) come to an opposite conclusion as to the rôle of pressure, on the basis of their experiments on the occlusion of hydrogen and oxygen by palladium.[1] They indicate that increase of hydrogen pressure up to 4.6 atmospheres at room temperature does not influence the amount of hydrogen adsorbed by palladium.

Reviewing the results of the recent investigations on the state of hydrogen adsorbed in palladium, in particular the results of investigations by Holt (4), Sieverts, Firth (2), McBain (5) and Müller and Schwabe (7), one may come to the conclusion that all data bespeak the fact that in all platinum metals hydrogen is primarily adsorbed, that at least in the case of palladium a solid solution is formed, and that no chemical composition occurs with any of the metals of this group.

In the case of adsorption of hydrogen by palladium, however, there is reason to assume a direct solubility of hydrogen, and therefore the adsorptive capacity of palladium must depend upon the pressure.

[1] The amount of oxygen present in palladium is less than the experimental error.

von Samson-Himmelstern (9), recalculating the data of Hoitsema (3) and Roseboom (8), comes to the conclusion that the relationship between the amount of hydrogen adsorbed by palladium and the pressure may be expressed by the following formula:

$$x = a \log p + b$$

where x = concentration of hydrogen dissolved, p = pressure, and a and b are constants. This equation he applied to the data of Roseboom, extended up to 1000 mm. of pressure. Extrapolating by his formula up to 1000 atmospheres of pressure, he obtains 0.787 gram-atom of hydrogen adsorbed per gram-atom of palladium If the extrapolation is made based on a linear relationship between the adsorptive capacity and the pressure, then 9 gram-atoms of hydrogen adsorbed per gram-atom of palladium are obtained at 1000 atmospheres and 25°C.

Experiments of von Samson-Himmelstern, who saturated palladium with hydrogen electrolytically, under a pressure of 1000 atmospheres, showed

TABLE 1

Adsorption of hydrogen by palladium

TEMPERATURE	PRESSURE OF HYDROGEN	HYDROGEN ADSORBED BY 119 G. OF PALLADIUM
degrees C.	*atmospheres*	*cc.*
420	80	2980
500	80	1900
420	120	3000

that almost no difference exists in the amount of hydrogen adsorbed by palladium at 1 and 1000 atmospheres. Thus, if at 1 atmosphere 1 gram-atom of palladium adsorbs 0.7 gram-atom of hydrogen, then at 1000 atmospheres the amount of hydrogen adsorbed again did not exceed 0.007 gram-atom of hydrogen per gram-atom of palladium. As we will see further, the part of pressure in the hydrogen adsorption by palladium is considerably greater than follows according to von Samson-Himmelstern.

Thus the survey of a small number of opinions on the question of the rôle of pressure in hydrogen adsorption by palladium permits the conclusion that there is no opinion in the literature actually based on experiments involving the application of high pressure. When the question arose, in connection with the work on displacement of noble metals from solutions of their salts by hydrogen under pressure, as to how much hydrogen might be adsorbed by palladium black and the state of this adsorbed hydrogen, we could find no answer in the literature and had to carry out a series of experiments under conditions which were to be used in further experiments on the displacement of palladium from solutions, namely, at intervals of

pressure from 1 to 25–50 atmospheres and at temperatures from 15°C. to 150°C.

EXPERIMENTAL PART

After a search for a suitable method for the determination of the adsorptive capacity of palladium for hydrogen under high pressure, a very simple equipment was adopted, which was essentially the ordinary Ipatieff's bomb, but of a diminished size (see figure 1).

The bomb was provided with an accurately controllable valve and with a manometer for accurate measurements up to 0.1 of an atmosphere.

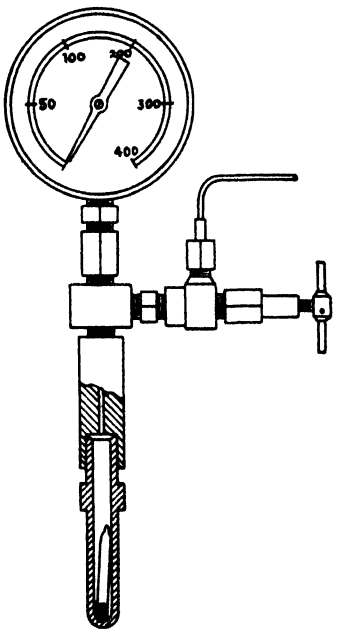

FIG. 1. IPATIEFF BOMB

Palladium was placed in the bomb in a sealed ampulla; hydrogen was pumped into the apparatus until a definite pressure was reached, then when the whole system was shown to be tight, the ampulla was broken by a slight shaking of the bomb. The contact of palladium with hydrogen pumped into the bomb resulted in a drop of pressure in the bomb, and in certain cases this drop reached a remarkable magnitude. The difference in readings before and after the experiment gave the total drop in pressure, and from the original volume of gas present in the bomb and the volume of the bomb itself, subtracting the volume of palladium and the glass of the ampulla, the amount of hydrogen adsorbed by the palladium was calculated.

The amount of gas pumped into the bomb by a given pressure was determined as follows: A definite pressure was produced in the bomb, for example, 20 atmospheres, and after testing the tightness for a day, the gas was discharged to a gasometer, a gas buret, or a gas meter. The volume of gas in cubic centimeters thus obtained by direct measurement corresponds to 19 atmospheres; from this the number of cubic centimeters corresponding to 1 atmosphere may be determined. A repeated determination of the number of cubic centimeters corresponding to 1 atmosphere, made at 5, 10, 15, and 20 atmospheres initial pressure, gave nearly an absolute check (the difference amounted to tenth parts of a centimeter), and thus indicated the correctness of readings of the measuring apparatus and the insignificant deviation of hydrogen from the ideal gas law.

Palladium black was prepared from a carefully purified palladium, according to Willstätter (10). The experiments were carried out as follows: After the sealed test tube containing the palladium was placed in the bomb and hydrogen pumped in, the bomb was tested for a while for tightness. In case the bomb was tight, the amount of hydrogen present in the bomb was determined by direct discharge. Afterwards hydrogen was pumped in again up to the former pressure and the tightness tested again.

After these preliminary tests the ampulla was broken by carefully inclining the bomb. Immediately after this, observation of the readings of the indicator on the manometer was started. The indicator moved rapidly at first, and then slowly in the direction of diminished pressure. In most cases the equilibrium was reached after two to three hours, while at low pressures, the equilibrium was established much more slowly.

The amount of gas adsorbed by palladium was determined by two methods: (1) By the difference in readings of pressure before the experiment and after. (2) By the difference between the amount of hydrogen pumped in the bomb and the amount of hydrogen discharged from the bomb after the experiment.

In the determination of the adsorptive capacity of palladium by the second method the question arises as to how fast the hydrogen, adsorbed at increased pressure, is given off at a decreased pressure. It was found that hydrogen, adsorbed by palladium under high pressure, was liberated extremely slowly after the pressure was decreased to 1 atmosphere. This is proved not only by direct observations, but also by a good correspondence in the results obtained by determination of the hydrogen adsorption by the first and second methods.

The following detailed description of one of the experiments is given as an example: 3 g. of palladium black were placed in a sealed ampulla having a volume of 16 cc. and an internal volume of 9.5 cc., and 10 atmospheres of hydrogen were pumped in. The amount of hydrogen taken corresponded to 440 cc. After testing for tightness the ampulla was

broken. The drop in pressure with time is shown in table 2. Calculation of the amount of hydrogen adsorbed by 3 g. of palladium at 3.5 atmospheres pressure gives 251 cc. according to the first method and 250 cc. according to the second method. Thus, the results practically coincide. The calculation of hydrogen adsorbed per gram-atom gives the following figures: 1 gram-atom of palladium adsorbs 0.79 gram-atom of hydrogen at 3.5 atmospheres pressure.

In further preliminary experiments according to the method described, various weights of palladium black (from 3 to 10 g.) and also various initial pressures of hydrogen from 7 to 40 atmospheres were applied, in order that the equilibrium hydrogen pressure would be established for such weights in the intervals of from 1 to 30 atmospheres.

TABLE 2

TIME AFTER BREAKING THE AMPULLA	PRESSURE
minutes	*atmospheres*
0	10
5	4.2
15	4.1
30	4.0
45	3.9
60	3.8
90	3.6
120	3.5
150	3.5
48 hours	3.5

Depending upon the weight of palladium and the initial hydrogen pressure, the pressure during the experiments decreased by from 10 to 20 atmospheres. The results of experiments carried out at 150°C. are shown in table 3.

It is seen from table 3 that under pressures above 1 atmosphere the solubility of hydrogen in palladium changes extremely slowly. Increasing the pressure twenty-seven times increases the solubility only 1.34 times. Thus the chief adsorptive capacity of pallladium lies within pressure limits of 1 atmosphere.

Attempts to apply the method used above for the determination of the adsorptive capacity at higher pressures failed, because the ampulla did not stand the high pressures and burst before the beginning of the experiment. Great difficulties were also encountered when working at high temperatures.

Thus the method had to be modified as follows (see figure 2): Instead of one bomb, two bombs with accurately measured volumes were used. Both

TABLE 3

Adsorption of hydrogen by palladium

EXPERIMENT NO.	WEIGHED AMOUNT OF PALLADIUM	INITIAL PRESSURE OF HYDROGEN	HYDROGEN PRESSURE AT THE END OF THE EXPERIMENT (EQUILIBRIUM)	HYDROGEN ADSORBED BY 1 CC. OF PALLADIUM	HYDROGEN ADSORBED BY 1 GRAM-ATOM OF PALLADIUM
	grams	*atmospheres*	*atmospheres*	*cc.*	*gram-atoms*
5	10.2	20	1.0	900	0.74
2	3	8	2.0	930	0.76
1	3	10	3.5	958	0.79
3	3	15	7.0	1000	0.82
4	10	30	8.5	1030	0.82
6	3.5	20	10.0	1055	0.83
7	10	40	14.0	1100	0.93
8	3.15	30	19.0	1160	0.96
9	3.10	40	27.0	1210	1.00

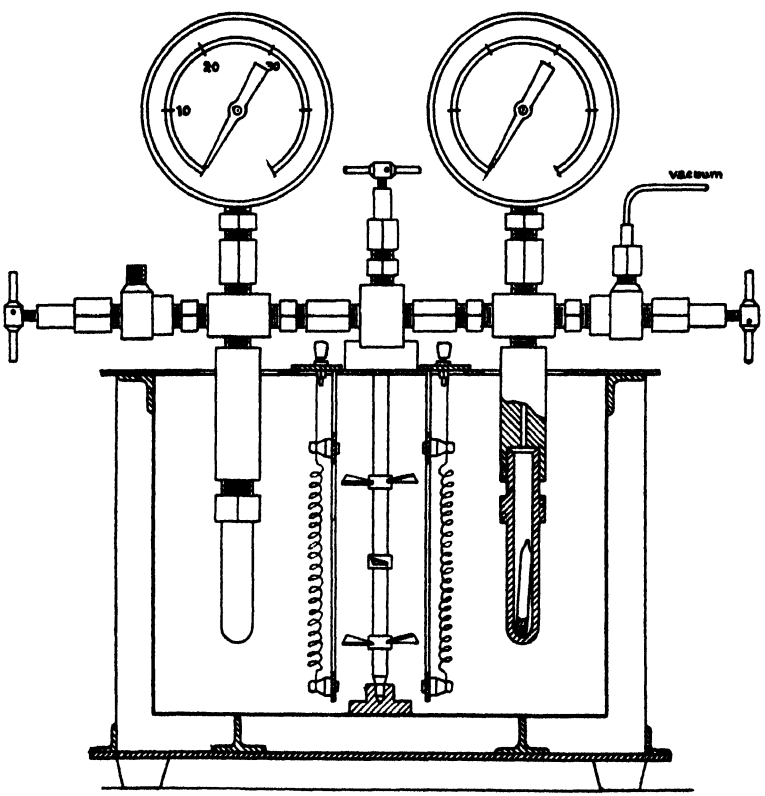

FIG. 2. BOMBS FOR ADSORPTION AT HIGH PRESSURES

bombs were connected with each other, so that by means of a proper turn of the valve, the pressure in one bomb could be controlled as desired, and in the other one a vacuum could be created, or by connecting both bombs, a constant pressure could be maintained in them for any desired time, without loss of gas. For the determination of the adsorptive capacity of palladium, the latter, accurately weighed and purified, was placed in a test tube in one of the bombs; after this the bomb was heated up to the required temperature (100–300°C.), connected with the vacuum pump, and maintained under a pressure of 1–2 mm. for 1 hour. If the bomb held the vacuum, then by a proper turn of the valve it was connected with the other bomb, which contained a definite amount of hydrogen under a definite pressure.

The amount of hydrogen was determined on the basis of the manometer readings, considering the free volumes of both bombs; at increased pressures, proper corrections for the deviation of hydrogen from the gas laws were introduced.

Applying the method described, determinations of the solubility of hydrogen in palladium were carried out at 25, 100, 150, 200, and 300°C. at pressures from 0.5 to 25 atmospheres.

Experiments at 25°C. were carried out in an isothermic room in which the temperature was maintained constant to within 0.1°C. The weight of palladium used was 9.2 g. The pressure of hydrogen in the bomb in which palladium was not present was 20 atmospheres. After testing the whole for tightness and after the vacuum of 1–2 mm. was observed to be constant in the bomb in which palladium was present, by opening the valve the first bomb was connected with the second, containing the palladium. The pressure in the first bomb was established at 10 atmospheres. After 24 hours a constant hydrogen pressure of 0.5 atmospheres was established in the second bomb containing palladium. The calculation shows that the amount of hydrogen adsorbed by 1 cc. of palladium equals 730 cc., or 1 gram-atom of palladium adsorbs 0.6 g. of hydrogen at 0.5 atmosphere.

Experiments at low pressures of hydrogen were carried out with the intention of checking the correctness of the method used and also to check data already existing in the literature for lower pressures. As the readings of the high pressure manometer could not be made accurately enough for the measurements of low pressures, after the pressure dropped in the bomb containing the palladium an ordinary mercury manometer was connected to it by means of a valve. As may be seen from the data and curve (table 4 and figure 3), the results obtained by us at low pressures agree with results obtained by other investigators.

Experiments at 100°C. and 150°C. were carried out in the same bombs in an oil thermostat with accurately regulated temperature. Thanks to

the high temperatures the equilibrium became established within a few hours (see tables 5 and 6).

The results of experiments at 25°, 100°, and 150°C. are illustrated in figure 3 in the form of curves.

TABLE 4

Solubility of hydrogen in palladium at 25°C. and various pressures

EXPERIMENT NO.	PRESSURE AT EQUILIBRIUM	AMOUNT OF HYDROGEN ADSORBED BY 1 CC. OF PALLADIUM	HYDROGEN ADSORBED BY 1 GRAM-ATOM OF PALLADIUM
	atmospheres	*cc.*	*gram-atoms*
1	0.5	730	0.60
2	1.0	785	0.65
3	2.0	845	0.70
4	4.5	860	0.71
5	10 0	940	0.77
6	20.0	1050	0.87

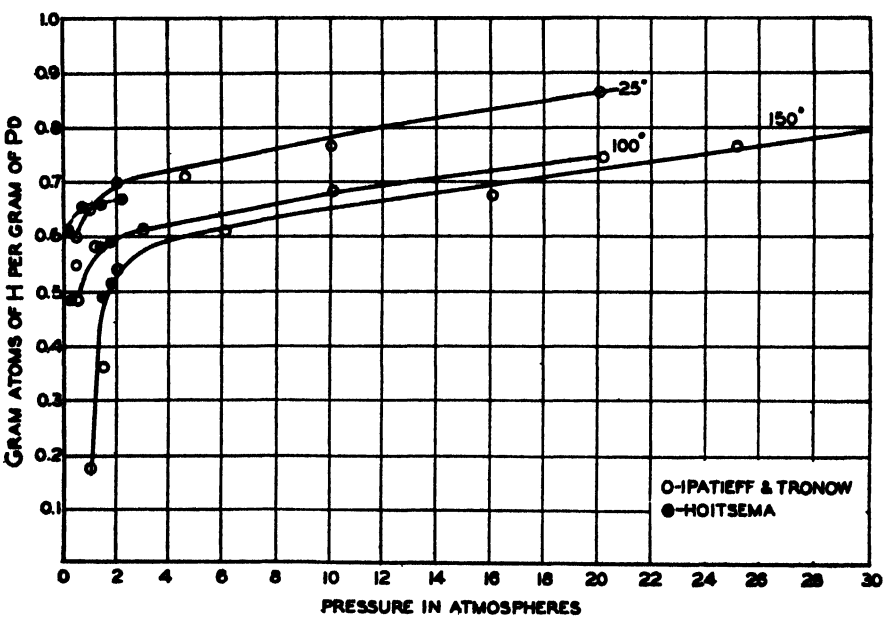

FIG. 3. RESULTS AT 25, 100, AND 150°C.

In these curves solid points correspond to the results of Roseboom, and circles show results obtained by us. As will be seen, the results agree well, also at low pressure. The curves have a peculiar character at each temperature with a sharp break at a pressure of about 1 atmosphere.

If the solubility of hydrogen in palladium is expressed not as a direct function of pressure, but as a function of the logarithm of pressure, then for the curve at 25°C. and 100°C. we obtain a straight line. The curve at 150°C. gives a straight line only beyond 2 atmospheres, because when passing from low pressures to high pressures, too sharp an increase in solubility occurs.

If we follow the curves in the direction of low pressures, obtained on the basis of results of other investigators, then three sections of the curves are

TABLE 5

Solubility of hydrogen in palladium at 100°C.

EXPERIMENT NO.	PRESSURE DURING THE EQUILIBRIUM	HYDROGEN ADSORBED PER 1 CC OF PALLADIUM	HYDROGEN ADSORBED PER 1 GRAM-ATOM OF PALLADIUM
	atmospheres	*cc*	*gram-atoms*
1	0.5	580	0.48
2	1.2	700	0.58
3	3 0	740	0.61
4	10.0	820	0 68
5	22	906	0 75

TABLE 6

Solubility of hydrogen in palladium at 150°C.

EXPERIMENT NO.	PRESSURE DURING THE EQUILIBRIUM	HYDROGEN ADSORBED PER 1 CC. OF PALLADIUM	HYDROGEN ADSORBED PER 1 GRAM-ATOM OF PALLADIUM
	atmospheres	*cc.*	*gram-atoms*
1	1	210	0.17
2	1.5	435	0 36
3	2	600	0 54
4	6.0	740	0.61
5	16	824	0.68
6	25	940	0.77

observed, as follows: The first section at very low pressures, in which a proportionality between solubility and pressure exists. These sections pass into the following, in which a sharp ascent of the curves is observed. This ascent might be explained either by the formation of a compound between palladium and hydrogen or by the formation of immiscible solid solutions.

Both these sections were studied in detail, and their study did not give a satisfactory explanation of the abnormal solubility of hydrogen in palladium. Neither did study of the third section, which is illustrated at each temperature by a logarithmic curve, give a final explanation of the question that interested us.

But even if a solid palladium hydride exists, then the stability of this compound should decrease with increase of temperature, and at a certain temperature no pressure could force hydrogen to combine with palladium. However, we know that two immiscible solutions may merge into one

TABLE 7

Solubility of hydrogen in palladium at 200°C.

HYDROGEN PRESSURE	HYDROGEN ADSORBED PER 1 GRAM-ATOM OF PALLADIUM
atmospheres	*gram-atoms*
1	0.002
3	0.042
4	0.077
5	0.183
6	0.32
7.5	0.40
17.5	0.44
26	0.56

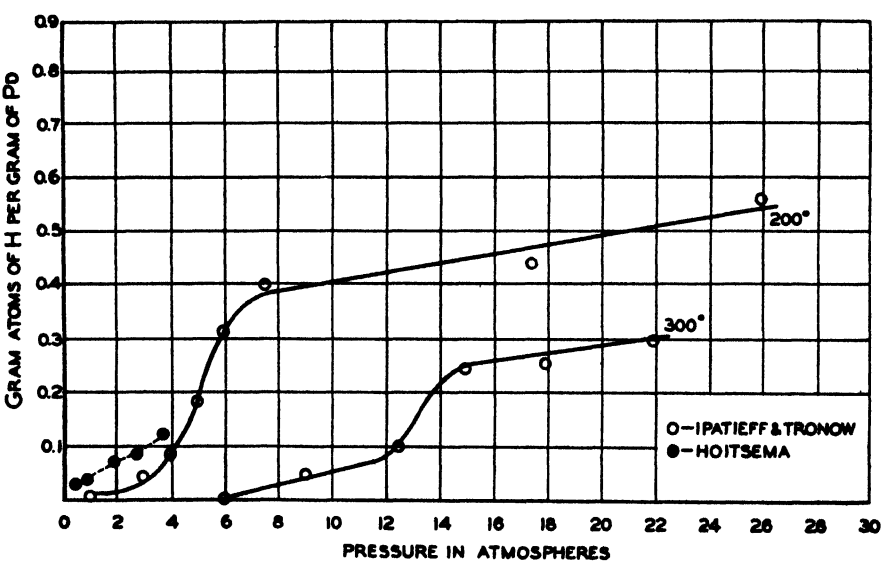

FIG. 4. RESULTS AT 200 AND 300°C.

solution with the increase of temperature. Thus we may draw the conclusion that in this and the other case a temperature will be reached at which the vertical sections of the curves of solubility of hydrogen in palladium disappear.

From the experiments of other writers we know that with increase of

temperature the parallel, vertical sections are displaced in the direction of an increased pressure and the length of the sections themselves decreases each time. For example, at 100°C. the break in the curve is observed at a pressure of less than 1 atmosphere, at 150°C. at a pressure of 1 to 2 atmospheres, and at 180°C. at 2 to 3 atmospheres.

At 200°C. Hoitsema did not reach a break because the pressure had to be elevated about 4 atmospheres and he did not have the necessary apparatus at his disposal. We succeeded in carrying out experiments at 200°C. and 300°C., and in this connection it should be noted that at 300°C. experiments were carried out in an air thermostat and therefore the data cannot be as accurate as at lower temperatures; probably this curve must be considered as corresponding to a lower temperature. The character of the curves for 200°C. and 300°C. is exactly the same as at lower temperatures (see table 7 and figure 4).

In all curves obtained at increased temperatures, the breaking point displaces in the direction of higher pressures. The so-called vertical part of the curve deviates more and more from the vertical. Considering further experiments at higher temperatures, it is evident that the curve of the relation between the solubility of hydrogen in palladium and pressure will change to a straight line.

Phenomena observed in the solubility of hydrogen in palladium recall the concept of gases at their critical temperature.

SUMMARY

1. The solubility of hydrogen in palladium black was determined at 15°, 25°, 100°, 150°, 200°, and 300°C. at pressures of from 1 to 27 atmospheres.

2. In agreement with data of Hoitsema, isotherms obtained are characterized by the presence of peculiar parallel parts, distinguishing hydrogen adsorption in palladium from other adsorption isotherms.

3. It is shown that with increase of temperature these parallel parts displace themselves in the direction of high pressures and begin to incline from the vertical; at 300°C. this tends to disappear and the whole curve becomes straightened out.

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THE INSERT GAS EFFECT IN THE RADIOCHEMICAL POLYMERIZATION OF ACETYLENE

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A recent paper on carbon dioxide as a radiochemical catalyst by Rosenblum (6) includes a few experimental results supplied by Lind and Bardwell concerning the rate of polymerization in a mixture of acetylene and carbon dioxide irradiated by alpha rays.

These results are found to agree with two formulas which I have deduced in 1931 and which were tested at first by means of the then available data on the catalytic effect of nitrogen in the same reaction (2).

In the case of the acetylene polymerization, the theory is very simple and may be summarized as follows. When acetylene is irradiated by β rays, every pair of ions produced in the gas causes the condensation of twenty-six molecules (3). This confirms the suggestion made by Rideal (5) that one layer of (n) neutral acetylene molecules clusters around every ion $C_2H_2^-$ or $C_2H_2^+$. The somewhat lower value $M/N = 20$, that has been found (1, 4) when acetylene is irradiated by α particles, may be explained by the increased rate of recombination which is to be anticipated in the case of intense and columnar ionization.

Let τ be the time required for the completion of a 13-molecular cluster, n_0 the initial number of ions per unit volume, n the ionization still remaining at the time τ. The bimolecular law that applies to ionic recombination, $dn/dt = -\alpha n^2$, yields the integrated formula

$$\frac{n}{n_0} = \frac{1}{1 + n_0\alpha\tau}$$

Now, the time τ required for complete clustering varies as the inverse of the acetylene concentration, while n_0 depends on the total pressure. Let p_1 and p_2 be the partial pressures of acetylene and of inert gas, let i_1 and i_2 be the respective molecular ionizations (i.e., total ionization times stopping power). Putting

$$Q_1 = i_1p_1 \quad \text{and} \quad Q_2 = i_2p_2$$

$$Y_1 = \frac{Q_1}{Q_2 + Q_1} \quad \text{and} \quad Y_2 = \frac{Q_2}{Q_1 + Q_2}$$

we shall write

$$\frac{n}{n_0} = \frac{1}{1 + A/Y_1}$$

The constant A is easily found if the lowering of M/N from 26 (β rays) to 20 (α rays) is ascribed entirely to the fact that a part of the recombination occurs before completion of the clusters. This assumption leads to the relations

$$\frac{M}{N} = 26\frac{n}{n_0} = \frac{26}{1 + A} = 20$$

$$A = 0.3$$

since, for pure acetylene, $Y_1 = 1$.

TABLE 1

p_1	p_2	M/N (experimental)	M/N (theoretical)
mm.	*mm.*		
557.5	561 5	16.39	16 0
460.3	550 5	16.38	15.4
436.1	547.8	15 15	15.2
413.5	545.2	13.82	15 1
349.9	538 0	13.02	14.4
304.9	533.0	12 82	13 9
200.3	521.3	10 78	12.1
171.1	517 9	10 78	11.4
133.0	517 6	10.08	10.2
95.9	509 5	8.6	8 6
25.4	501.5	3.1	3.3

Using this value of A and putting $i_1 = 1.4$ and $i_2 = 1.52$, the formula that should apply in the case of the polymerization of acetylene mixed with carbon dioxide can be written as follows

$$\frac{M}{N} = \frac{26}{1 + 0.3\dfrac{1.4p_1 + 1.52p_2}{1.4p_1}}$$

The first three columns of table 1 give p_1, p_2, and the corresponding experimental values of M/N (calculated by Lind and Bardwell for 100 per cent ionic efficiency of the catalyst). The fourth column gives the theoretical values of M/N from the above formula.

There is still another feature of interest about the polymerization of acetylene mixed with carbon dioxide. A small amount of the latter disappears from the gaseous phase, but can be partially recovered on heating

the solid. In the experiment of Lind and Bardwell the amount of missing carbon dioxide that was not recovered corresponded to a partial pressure of 63 − 35 = 28 mm. Nitrogen shows a similar behavior, which has been explained (3) by the assumption that a nitrogen ion may be found in the center of a cluster just as well as a positive or negative acetylene ion.

It is easy to calculate the amount of carbon dioxide that should disappear if among the positive ions the percentage of carbon dioxide were equal to $Y_2 = Q_2/(Q_1 + Q_2)$ and if among the negative ions the percentage of CO_2^- were equal to $Z_2 = R_2/(R_1 + R_2)$. In the latter expression, $R_1 = 28.5 \times 10^{-16}\, p_1$ and $R_2 = 24.4 \times 10^{-16}\, p_2$, where 28.5×10^{-16} and 24.4×10^{-16} are the squares of the critical radii that may be obtained from the dielectric constants 1.00134 and 1.00098. The small variation of pressure of carbon dioxide is then expressed by the equation

$$-\,dp_2 = \frac{p_2}{26}\left(\frac{1.52}{1.40}\ln\frac{1}{Y_2} + \frac{24.4}{28.5}\ln\frac{1}{Z_2}\right)$$

Y_2 and Z_2 being calculated from initial conditions. (For the deduction of the formula see reference 3). Using the numerical values quoted by Rosenblum we find $-\,dp_2 = 29.3$ mm.

The agreement with the experimental value of 28 mm. is quite satisfactory. It might have been improved by taking into account the variability of p_2 when calculating Y_2 and Z_2.

SUMMARY

A theory previously developed is shown to be consistent with recently published data concerning the inert gas effect in the radiochemical polymerization of acetylene.

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THE SOLUBILITIES OF CALCIUM HYDROXIDE, CALCIUM IODATE, AND AMMONIUM PERCHLORATE IN DILUTE AMMONIACAL SOLUTIONS

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In a previous paper (6) it has been mentioned that the effect of ammonia upon the adsorption of calcium hydroxide from aqueous medium by silica gel and hydrous oxides is not to be attributed to a complex formation between calcium hydroxide or calcium ions and ammonia. More definite proof of this statement was obtained from solubility measurements of calcium hydroxide in solutions having a concentration up to 2 *N* in ammonia. Since ammonia appeared to have a marked lowering affect upon the solubility of calcium hydroxide, it was decided to determine the solubilities of calcium iodate and of ammonium perchlorate in the same media.

MATERIALS USED

Calcium oxide. A hot solution of C.P. calcium chloride was treated with a slight excess of a solution of ammonium oxalate. The precipitate was digested, filtered, washed until free from chloride, dried and ignited in an electric furnace.

Calcium iodate, $Ca(IO_3)_2 \cdot 6H_2O$. A hot solution of C.P. calcium chloride was treated with a slight excess of potassium iodate. The precipitate, after washing, was twice recrystallized from conductivity water. Upon drying at 110°C. the monohydrate is formed. On shaking with water or dilute ammonia solution it is quickly transformed into the hexahydrate.

Ammonium perchlorate. A Kahlbaum product recrystallized from water was used.

Ammonia. A solution of carbonate-free ammonia was obtained by distillation of 20 per cent ammonia in the presence of an excess of barium hydroxide. The distillate was kept in a paraffined container and protected from carbon dioxide of the air.

SOLUBILITY DETERMINATION

Solubilities were determined in a thermostat at 25.00°C. ± 0.02°C. Paraffined containers were used throughout this work, although with glass-stoppered Pyrex bottles the same results were found. In all cases equilibrium was attained after fourteen to twenty hours of shaking. The pre-

cipitates were then allowed to settle in the thermostat and samples of the supernatant liquids analyzed.

TABLE 1

Solubility of calcium oxide in ammoniacal solutions at 25°C.

CONCENTRATION OF NH_3	DENSITY OF SATURATED SOLUTION AT 25°C.	CONCENTRATION OF CALCIUM HYDROXIDE		
		Moles per liter	CaO per 100 cc. of solution	CaO per 100 solution
N			*grams*	*grams*
0	0 998	0 02128	0.1194	0.1196
0.496	0.994	0 01993	0 1117	0 1124
0.981	0 989	0 01850	0 1038	0.1049
1 475	0.985	0 01700	0.0953	0 0967
1.955	0.982	0.01571	0.0881	0 0896

TABLE 2

Solubility of calcium iodate hexahydrate in ammoniacal solutions at 25°C.

CONCENTRATION OF NH_3	DENSITY OF SATURATED SOLUTION AT 25°C.	CONCENTRATION OF $Ca(IO_3)_2$		
		Moles per liter	$Ca(IO_3)_2$ per 100 cc of solution	$Ca(IO_3)_2$ per 100 g of solution
N			*grams*	*grams*
0	0.999	0.00785	0.306	0.306
0 489	0.995	0.00779	0 304	0.305
0.986	0.991	0 00756	0 295	0 298
1.422	0.987	0 00733	0 285	0 289
1.966	0.983	0 00715	0 279	0 284

TABLE 3

Solubility of ammonium perchlorate in ammoniacal solutions at 25°C.

CONCENTRATION OF NH_3	DENSITY OF SATURATED SOLUTION AT 25°C	CONCENTRATION OF NH_4ClO_4		
		Moles per liter	NH_4ClO_4 per 100 cc of solution	NH_4ClO_4 per 100 g. of solution
N			*grams*	*grams*
0	1.095	1.830	21 50	19 64
0.443	1.092	1.841	21 63	19.81
0.876	1.089	1.871	21 98	20 16
1 303	1.088	1.915	22.50	20.68
1 731	1 086	1 954	22 96	21.14
2 59	1 084	2 049	24.08	22 23

ANALYSES

In the solubility determinations of calcium hydroxide the calcium and hydroxide content was determined. After removing the excess ammonia,

the calcium was precipitated from weakly acid solution as oxalate, and titrated according to standard procedures with potassium permanganate. Other samples were evaporated to dryness, the residues treated with an excess of standard hydrochloric acid, carbon dioxide driven off by boiling, and the acid back-titrated with sodium hydroxide, using methyl red as indicator. The results obtained in both procedures agreed within 0.5 per cent, the oxidimetric method always yielding higher values than the acidimetric one. The solubility of calcium iodate was found from iodometric titrations of the iodate. The ammonium perchlorate content of the solutions was determined by evaporating known volumes to dryness and weighing after drying to constant weight at 110°C. All analyses have been made in duplicate or triplicate. Duplicate analyses with samples from the same bottle agreed within 0.1 per cent in the case of ammonium perchlorate; with samples from different bottles discrepancies of the order of 1 per cent were sometimes noticed. Therefore the solubility data given for ammonium perchlorate do not seem to be as exact as those of the other two substances. The highest values obtained are reported in table 3. In all cases the densities of the supernatant liquids were determined at 25°C. Correspondingly the solubilities found are expressed in moles per liter and in grams per 100 g. and per 100 cc. of solution.

RESULTS

The results are given in tables 1, 2, and 3.

DISCUSSION OF THE RESULTS

1. *Solubilities in water.* Data reported in the literature on the solubility of calcium oxide in water vary from 0.115 to 0.125 g. of CaO per 100 cc. at 25°C. (cf. Seidell, 1928). In a recent paper Johnston and Grove (5) gave results obtained with crystalline calcium hydroxide, which are 7.5 per cent lower than the figure obtained with our product. The difference is probably due to the difference in the nature of the saturating phases used.

The values obtained with our product of calcium oxide were quite reproducible and independent of the amount of solid taken. The solubility of calcium iodate hexahydrate agrees exactly with the figure determined by Hill and Brown (3). Their paper was published after this work had been finished. There is a wide divergency in the literature on the solubility of ammonium perchlorate in water; expressed in grams of NH_4ClO_4 per 100 g. of solution the following data at 25°C. are reported 21.1 (Carlson (1), by interpolation); 19.8 (Mazzuchelli and Rosa (8) by interpolation), 20.02 (Freeth (2), at 25°C.); 19.95 (Willard and Smith (10), at 25°C.). The figure of 19.64 determined in this study is lower than any of the pre-

vious values reported, but was found to be consistent with various times of shaking and different amounts of solid body.

2. The effect of ammonia upon the solubilities of the three substances investigated is quite different. The solubility of ammonium perchlorate increases regularly with increasing ammonia concentration in the solution, that of calcium iodate hexahydrate decreases slightly, and that of calcium hydroxide very markedly. Konowalow (7) at 20°C. found 0.1017 g. of calcium oxide per 100 cc. of water, and 0.0610 g. per 100 cc. of solution containing 5.2 per cent of ammonia (about 3 N).

From the results given in table 1 it may be concluded that up to a concentration of 2 N in ammonia the solubility of calcium oxide decreases linearly.

$$S = 0.1194 - 0.016\, C_{NH_3}$$

S is solubility expressed in grams of CaO per 100 cc. of solution at 25°C.; C_{NH_3} is the normality of ammonia.

The decrease of the solubility of calcium hydroxide in the presence of ammonia cannot be attributed to a common ion effect. For example, in a solution 1 N with respect to ammonia and saturated with lime, the concentration of the hydroxyl ions contributed by the ammonia is only 1.3 per cent of that formed by dissociation of the calcium hydroxide. The decrease of the solubility of calcium hydroxide in the presence of ammonia therefore has to be attributed to a specific medium effect. Ammonia at 24.5°C. has a dielectric constant (4) of 14.9 and is therefore expected to decrease markedly the dielectric constant of aqueous solutions, and consequently the dissociation of electrolytes. It should be remembered that the second dissociation of calcium hydroxide is far from being complete; in the presence of ammonia it is still further decreased and consequently the solubility also. Qualitatively speaking, ammonia has here the same effect as organic solvents, such as methanol, ethanol, etc., have on the dielectric constant of aqueous solutions. It is beyond the scope of this paper to investigate in further detail the striking effect of ammonia upon the solubility of calcium oxide.

3. The results obtained confirm the primary object of this investigation, namely, to prove that the effect of ammonia on the adsorption of calcium hydroxide by hydrous oxides and silica gel is not to be attributed to a complex formation. The linear decrease of the solubility with the ammonia concentration and the constant composition of the solid show definitely that up to concentrations of 2 N in ammonia no complexes are formed in the solution.

SUMMARY

1. The solubilities of calcium hydroxide, calcium iodate, and ammonium perchlorate at 25°C. in water and in solutions containing concentrations of ammonia up to 2 N have been determined.

2. The solubility S (in grams of CaO per 100 cc. of solution at 25°C.) of calcium hydroxide decreases linearly with increasing ammonia concentration:

$$S = 0.1194 - 0.016\, C_{NH_3}$$

3. No complex compounds between calcium hydroxide or calcium ions and ammonia are formed in the solution at ammonia concentrations smaller than 2 N.

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THE OSMOTIC PROPERTIES OF COLLOIDAL ELECTROLYTES AND THE HAMMARSTEN EFFECT

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I. NATURE OF THE PROBLEM

The vast literature on colloidal electrolytes suffers, more perhaps than most chapters of physical chemistry, from a lack of correlation in the light of exact theories. Thermodynamic concepts such as activity and osmotic coefficients are often misused and, whenever the ideas of the interionic attraction theory are applied, the reasonings are of an entirely qualitative nature. We refer the reader to the book of Pauli and Valkò (8) where most papers on the subject are discussed, briefly reviewed, or at least quoted. Theoretical treatments so far proposed are either too specialized or too vague. On the other hand, the general mathematical treatment of Scatchard and Kirkwood (9), which implicitly includes the case of colloidal electrolytes, is prohibitively complicated for most physically significant cases. The so-called "Hammarsten effect" gave rise to a qualitative theoretical treatment by E. and H. Hammarsten (4, 5) and to a general theory by Linderström-Lang (7). According to Pauli and Valkò (8) a colloidal electrolyte exhibits the Hammarsten effect when its osmotic pressure is smaller than that calculated for a concentration equal to the activity of the simple ions, i.e., when, in the case of an acid for instance,

$$P < a_{H^+} \cdot RT \tag{1}$$

P is the measured osmotic pressure, a_{H^+} the activity of the hydrogen ion, R, the molar gas constant, and T the absolute temperature.

Let us recall in this connection that activities do not bear a direct relation to the osmotic pressure, except for the fact that there are thermodynamic differential relations between activity and osmotic coefficients. If g_0 is the osmotic coefficient of the solvent and f_s the activity coefficient of the solute, we have

$$N_0 d\left\{(1 - g_0) \log \frac{1}{N_0}\right\} = - N_s d \log f_s \tag{2}$$

N_0 and N_s being the mole fractions of the solvent and the solute, respectively.

In the case of dilute solutions we may define the osmotic coefficient as the ratio between the observed osmotic pressure P and that calculated according to the formula

$$P_c = mRT \tag{3}$$

m being the concentration in moles per liter. We have then

$$P = gP_c = gmRT \tag{4}$$

The abnormality corresponding to the Hammarsten effect is that g defined as above is often of the order of 1 or less when, on account of dissociation, one would expect much higher values.

The low osmotic pressures exhibited by many colloidal electrolytes suggest immediately the presence of ions of very high valence such as those which would result from the association of a large number of simple ions into colloidal micelles. It is then natural to investigate the properties of these systems by means of the theory of electrolytes. We shall assume that all micelles have the same charge $z\epsilon$, ϵ being the elementary quantum of electricity. We thereby overlook the possible presence of micelles of different charges or that of neutral aggregates. The charge and size of the micelle should then be considered as averages. Furthermore, we shall restrict our reasoning to cases where the oppositely charged particles are monovalent single ions. Supposing that in dilute solutions the cohesive forces have no appreciable effect once the micelles are formed, our problem is reduced to a study of the properties of an electrolyte of valence type 1-z according to the Debye-Hückel theory.

II. OSMOTIC PROPERTIES OF AN ELECTROLYTE OF VALENCE TYPE 1-z ACCORDING TO THE DEBYE-HÜCKEL THEORY

The solution contains n free monovalent ions and n/z ions of valence z per cubic centimeter. The charge $z\epsilon$ of the latter is supposed to be concentrated in such a way that the distance of closest approach between the monovalent ions and the ions of valence z is a A.U. The electric fields of both kinds of ions are supposed to possess spherical symmetry.

The Debye-Hückel theory (2, 6) defines as follows the "characteristic length" or radius of the ionic atmosphere $1/\kappa$:

$$\kappa = \sqrt{\frac{4\pi\epsilon^2}{DkT}\cdot\Sigma n_r z_r^2} \tag{5}$$

D is the dielectric constant, k is Boltzmann's constant, n_r the number of ions r per cubic centimeter, and z_r the valence of these ions. Here we have

$$\Sigma n_r z_r^2 = n + \frac{n}{z}\cdot z^2 = n(z+1) \tag{6}$$

The ionic strength I of the solution is

$$I = \frac{1}{2} \cdot \frac{1000}{N_A} \cdot \Sigma n_r z_r^2 \tag{7}$$

N_A being Avogadro's number.

In our case,

$$I = \frac{1}{2} \cdot \frac{1000}{N_A} \cdot n(z + 1) \tag{8}$$

Calling C the concentration of the monovalent ions in moles per liter, we have

$$I = \frac{1}{2} C(z + 1) \tag{9}$$

It will be sufficiently accurate for our purpose to suppose that the product DT, in the case of water, is constant in the range of temperature in which most experimental data are obtained (0 to 25°C). We have then

$$\kappa = 0.23 \sqrt{C(z + 1)} \cdot 10^8 \tag{10}$$

Defining the osmotic coefficient g of the solvent as the ratio between the actual osmotic pressure and that of an ideal solution of concentration $C\ (1 + \frac{1}{z})$ we have

$$1 - g = 0.26\omega \sqrt{C\left(1 + \frac{1}{z}\right)} \cdot \sigma(\kappa a) \tag{11}$$

with

$$\omega = \left(\frac{\Sigma \nu_r z_r^2}{\nu}\right)^{3/2} \tag{12}$$

ν_r being the number of ions r into which one molecule of salt dissociates, and ν the total number of ions. Here we have

$$\omega = \left(\frac{1 + \frac{1}{z} z^2}{1 + \frac{1}{z}}\right)^{3/2} = z^{3/2} \tag{13}$$

$\sigma(\kappa a)$ is a function of the product κa defined as follows:

$$\sigma(\kappa a) = \frac{3}{(\kappa a)^3}\left[1 + \kappa a - \frac{1}{1 + \kappa a} - 2 \log (1 + \kappa a)\right] \tag{14}$$

In the first paper of Debye and Hückel (2) a table of the numerical values of σ is given.[1]

The ratio between the actual (or observed) osmotic pressure and that of the corresponding ideal undissociated solute is usually given in experimental papers. A definite formula is then assumed for the solute and the concentrations are expressed in moles per liter in terms of that formula. It is more logical to express the concentrations in moles or gram equivalents of the simple ion (Na^+, Cl^-, . . .) per liter (C in our notation).

From equations 11 and 13 we deduce for the osmotic pressure

$$P = gP_{\text{id.}} = P_{\text{id.}}[1 - 0.26z\sqrt{C(1+z)}\cdot\sigma(\kappa a)] \tag{15}$$

The ideal osmotic pressure $P_{\text{id.}}$ is given by

$$P_{\text{id.}} = C\cdot\frac{1+z}{z}\cdot RT \tag{16}$$

Combining formulas 15 and 16 we find

$$P = CRT\cdot\frac{1+z}{z}[1 - 0.26z\sqrt{C(1+z)}\cdot\sigma(\kappa a)] \tag{17}$$

Formulas analogous to formula 15 could of course be obtained for the freezing point lowering, the dew point lowering, etc.

III. INTERPRETATION OF SOME TYPICAL EXPERIMENTAL DATA

On the basis of the foregoing considerations it is possible to attempt an interpretation of experimental data. Two parameters have to be chosen: z and a. It is quite likely that both these parameters change appreciably with concentration. We shall however show that if z is supposed to be constant, it is possible to find a particular value of z such that the corresponding values of a do not change too much with concentration.

Our procedure is the following: The values of g are computed at the various concentrations for which data are available. It is then shown that the lowest value of z compatible with the probable formula of the compound under consideration (2 for Congo red, 4 for sodium thymonucleate) yields too high values of g and that association of ions of one sign has to be assumed. Various successive values of z, all multiples of the lowest (4, 6, ... for Congo red, 8, 12, ...for sodium thymonucleate) are used until a value is found which gives a $\sigma(\kappa a)$ smaller than one at the lowest concentration at which data are available. The values of $\sigma(\kappa a)$ at the various concentrations are then deduced from the calculated values of g, using formula 15 and the corresponding values of κa are obtained from a smooth curve

[1] The value 0.855 given in the table for $x = 0.1$ is wrong and should be replaced by 0.866.

drawn by means of the values of κa and $\sigma(\kappa a)$ given by Debye and Hückel (2). κ is calculated by means of formula 10 and a is then obtained. There seems to be one particular value of z for which a is sufficiently constant and such that $\sigma(\kappa a)$ is smaller than 1 at the lowest concentration. (Values of $\sigma(\kappa a)$ larger than 1 correspond to negative values of a.)

These calculations are only of an approximate nature for the following reasons:

1. They are based on a rather crude model (spherical symmetry of the electric field due to the charges).
2. The values of κa become larger than 1 already at very low concentrations. The model and calculations of the Debye-Hückel theory of course lose much of their plausibility when the distance of closest approach of two ions of opposite signs becomes larger than the radius of the ionic atmosphere of either one.
3. The higher terms of the Poisson-Boltzmann equation are neglected.

TABLE 1

Osmotic pressure of Congo red (Donnan and Harris)

$T = 290°$

C EQUIVALENT OF Na^+ PER LITER	P_{calcd} (calculated)	P (measured)	$P/P_{calcd.}$
0.17324	1567 0	1363	0 869
0 14404	1304 0	1139	0.873
0 04742	676 0	603	0 890
0.03664	331 8	310	0.934
0 02170	196 0	185.5	0 950
0.01112	100.5	97	0 965

We now give the results obtained in two typical cases: aqueous solutions of Congo red (Donnan and Harris (3)) and of sodium thymonucleate (E. Hammarsten (4)).

A. Congo red

Table 1 gives the concentration C of Congo red in equivalents of sodium ion per liter, the osmotic pressure calculated for an ideal solution of the compound Na_2Co (molecular weight, 696) in millimeters of mercury, the observed osmotic pressure P in millimeters of mercury, the ratio $P/P_{calcd.}$. The table is taken from Zsigmondy (10). This table shows that the observed osmotic pressure is smaller than that corresponding to an undissociated solute of formula Na_2Co and hence that highly charged micelles are probably present.

For $z = 2, 4$, and 6 the value of $\sigma(\kappa a)$ corresponding to the lowest con-

centration is larger than 1. We have calculated $\sigma(\kappa a)$, κa, κ and a for $z = 8$, 10, 12, and 14, respectively. The values of a are plotted against the concentration on figure 1 for these four values of z. The curve corresponding to $z = 10$ seems the most satisfactory. The small values of a obtained at the lower concentrations may be due to the neglect of the higher terms. We feel justified however in concluding that the anions of Congo red solutions consist of four or five simple double-charged anions $Co^{=}$.

B. Sodium thymonucleate

The osmotic properties of this salt were carefully studied by E. Hammarsten (4). The results are particularly suitable for an interpretation ac-

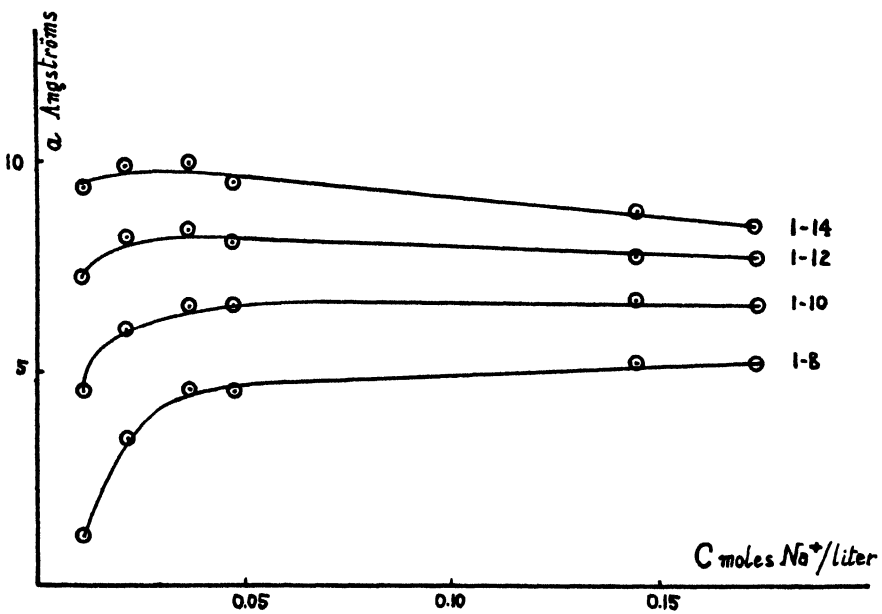

FIG. 1. MEAN IONIC DIAMETERS OF CONGO RED FOR DIFFERENT CHARGES OF THE MICELLES

cording to our method: all the data were obtained at extremely low concentrations, the range being 0.33×10^{-3} to 9×10^{-3} moles per liter (empirical formula of the salt, Na_4T), hydrolysis is apparently negligible, and dissociation is probably very high. Our interpretation will be based, as in the case of Congo red, on the assumption that all the sodium ions are unbound. The molecular weight corresponding to the formula Na_4T is 1545. Table 2 gives the concentrations C of the sodium ion in equivalents per liter, the osmotic pressure $P_{calcd.}$ calculated for an ideal solution of molality $C/4$ in centimeters of water, the observed osmotic pressure P in centimeters of water, the ratio $P/P_{calcd.}$.

TABLE 2

Osmotic pressure of aqueous solutions of sodium thymonucleate (E. Hammarsten)
$T = 293°$

C EQUIVALENT OF Na^+ PER LITER	P_{calcd} (calculated)	P (observed)	$P/P_{calcd.}$
	cm H_2O	*cm.* H_2O	
1.32	8 1	6 5	0.80
2.52	15 6	13.0	0.83
5.12	31.7	25 0	0.79
6.32	39.2	31 0	0.79
9.68	59 9	47.7	0.79
14.28	88 5	69.0	0.78
17.12	106.1	82 5	0 78
17 20	106.6	83.1	0.78
17.52	108 5	83.5	0.77
16 40	101.4	82.0	0 81
18 08	111.8	85.6	0.77
18.00	111.3	85.8	0.77
18 00	111 3	86.5	0.78
36 00	222 7	173 2	0.78

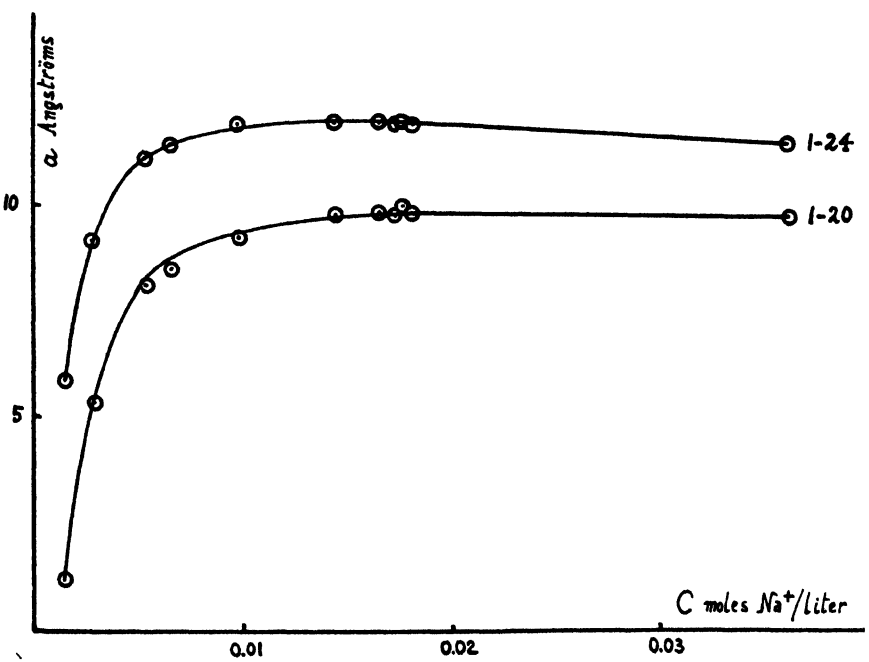

FIG. 2. MEAN IONIC DIAMETERS OF SODIUM THYMONUCLEATE FOR TWO DIFFERENT CHARGES OF THE MICELLES

The ideal osmotic pressure $P_{id.}$ of a completely dissociated salt of concentration $C\ (1 + \frac{1}{z})$ is given by formula 16.

We have here

$$P_{calcd.} = \frac{1}{4} CRT \tag{19}$$

and

$$P_{id.} = 4P_{calcd.} \frac{1+z}{z} \tag{20}$$

The other formulas to be used in the calculations are the same as those used in the case of Congo red (formulas 15, 16, 17, 10, etc.).

The ratios $P/P_{calcd.}$ fluctuate irregularly but are practically constant. We are hence justified in considering that, at all concentrations investigated, the ratio $P/P_{calcd.}$ is equal to the average value 0.78.

We have to go to as high as $z = 20$ before obtaining a value of $\sigma(\kappa a)$ smaller than 1 at the lowest concentration. We have calculated $\sigma(\kappa a)$, κa, κ and a for $z = 20$ and 24. The values of a are plotted against the concentration on figure 2. The curve for $z = 20$ is a little more satisfactory than that for $z = 24$. The small values of a obtained at the lower concentrations and the large values of κa (which become already larger than 1 at concentrations of the order of 10^{-2} moles per liter) show that we are far from the ideal conditions where the Debye-Hückel theory can be considered as correct. It is however reasonable to conclude that the anions of sodium thymonucleate consist of at least five simple quadruple-charged ions.

We have also made calculations of the same type for the other thymonucleates studied by E. Hammarsten and for certain colloidal dyes studied by Biltz (1). The results were analogous to those presented here.

SUMMARY

It is shown that, if the proper amount of association into micelles is taken into account, the low osmotic pressures observed for several colloidal electrolytes are qualitatively explained by the Debye-Hückel theory. The Hammarsten effect is not an unexpected "abnormality."

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IONIZATION BY ALPHA PARTICLES IN GASEOUS MIXTURES

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INTRODUCTION

Two methods of calculation of the ionization by alpha particles from radon have been developed,—the average path method of Lind (5) and a method due to Mund (6). These calculations have been the subject of former studies (3, 4). Whereas the average path method which involves the molecular ionization is directly applicable to the case of gaseous mixtures, it is necessary to develop a method of computing the relative total ionization for mixtures before the Mund method can be applied to them. Such calculations are presented in this paper. The following symbols are used:

I_T = total ionization (number of ion pairs) produced by an alpha particle from radon in its range (r_0) in air at standard conditions (1.55×10^5 ion pairs).

$\bar{I}$ = average intensity of ionization in air at N.T.P.

I_i = total ionization produced by an alpha particle on gas i in the mixture.

N = number of alpha particles formed in time t.

F' = Mund's correction factor (see references 3 and 4).

r_0 = range of the alpha particle from radon in air at N.T.P. (concordant range = 3.45 cm.; references 3 and 4).

r_i = range of alpha particle in gas i at the temperature of the experiment and at a pressure P equal to the total pressure of the mixture.

x_i = distance traversed by the alpha particle.

y_i = x_i/r_i = reduced distance.

$\bar{x}$ = average path of the alpha particle.

ρ = ratio of r_m to radius of reaction vessel.

E_T = total kinetic energy of the alpha particle.

E_i = energy of the alpha particle at the point x_i.

g_i = total ionization relative to air (N.T.P.) in gas i due to one alpha particle.

P_i = partial pressure of gas i.

P = total pressure of the gaseous mixture.
S_i = stopping power of gas i.
t = temperature of the experiment (°C.).
m = as subscript refers to the gaseous mixture.

I. ENERGY LOSS AND TOTAL IONIZATION PER CENTIMETER PATH

These two quantities are given by

$$dE_i = \frac{2}{3}\frac{E_i}{r_i}\left(1 - \frac{x_i}{r_i}\right)^{-1/3} dx_i \tag{1}$$

$$dI_i = \frac{2}{3}\frac{g_i I_T}{r_i}\left(1 - \frac{x_i}{r_i}\right)^{-1/3} dx_i \tag{2}$$

The integrated forms of these equations as a function of the reduced path (x_i/r_i) are:

$$E_i = E_T\left(1 - \frac{x_i}{r_i}\right)^{2/3} = E_T(1 - y_i)^{2/3} \tag{3}$$

$$I_i = g_i I_T\left(1 - \frac{x_i}{r_i}\right)^{2/3} = g_i I_T(1 - y_i)^{2/3} \tag{4}$$

From equations 3 and 4 it is seen that at the same value of the ratio "y" the alpha particle has lost the same fraction of its energy, and similarly the same fraction of its total ionization has been produced when it has travelled the distance x_i in the separate gases. The alpha particle travels in the gaseous mixture, however, and in order to deal with this situation it is convenient to consider the case in the following manner.

II. THE STRIATED GAS

For convenience of discussion a differential element of the gaseous mixture may be thought to consist of i layers of gas which are traversed by the alpha particle in succession. These i layers have together the elementary length dx_m. All of the molecules of type i are separated into the layer dx_i such that

$$\frac{P_i}{P} dx_m = dx_i \tag{5}$$

and

$$\sum \frac{P_i}{P dx_m} = \Sigma dx_i = dx_m \tag{6}$$

This means that each of the individual gases has the pressure P in dx_i. This separation of dx_m into elements dx_i is very helpful in studying the

problem. In order to be certain that the treatment below is satisfactory, a graphical study was made for the case of two components. The gas was divided into alternating layers of gas 1 and gas 2, and it became clear that the following discussion adequately represents the case of mixtures.

III. THE RANGE AND STOPPING POWER OF A GAS MIXTURE

The loss of energy by the alpha particle in a gaseous mixture of length dx_m is the sum of the losses (dE_i) due to the ionization of the various gases. This loss is also represented by an expression similar to equation 1 with *the range in the mixture* r_m replacing the range r_i. Using equation 1:

$$\sum \frac{2}{3} \cdot \frac{E_T}{r_i}\left(1 - \frac{x_i}{r_i}\right)^{-1/3} \cdot \frac{P_i}{P}\, dx = \frac{2}{3}\frac{E_T}{r_m}\left(1 - \frac{x_m}{r_m}\right)^{-1/3} \cdot dx \tag{7}$$

But this comparison must be made at the same point on the reduced path

$$\frac{x_1}{r_1} = \frac{x_2}{r_2} = \ldots \frac{x_i}{r_i} = \frac{x_m}{r_m} \tag{8}$$

Therefore

$$r_m = \frac{P}{\sum \frac{P_i}{r_i}} \tag{9}$$

but

$$r_i = \frac{r_0}{S_i P} \qquad \text{and} \qquad r_m = \frac{r_0}{S_m P} \tag{10}$$

therefore

$$S_m = \frac{\Sigma P_i S_i}{P} \tag{11}$$

The last result is equivalent to the usual statement that stopping powers are additive in the case of mixtures.

IV. THE RELATIVE TOTAL IONIZATION IN A GAS MIXTURE

By a similar argument the total relative ionization (g_m) in a mixture may be defined. The sum of the ionizations (dI_i) in each layer (dx_i) must be equal to the ionization in the layer dx_m. Using equation 2:

$$\sum \frac{2}{3}\frac{g_i I_T}{r_i}\left(1 - \frac{x_i}{r_i}\right)^{-1/3} \cdot \frac{P_i}{P}\, dx = \frac{2}{3}\frac{g_m I_T}{r_m}\left(1 - \frac{x_i}{r_m}\right)^{-1/3} \cdot dr \tag{12}$$

and with equation 8

$$\sum \frac{g_i P_i}{r} = \frac{g_m P}{r_m} \tag{13}$$

substituting from equation 9 and 10

$$g_m = \frac{\Sigma g_i S_i P_i}{\Sigma P_i S_i} \tag{14}$$

The only case where this result can be checked with experiment is that of air where the proper values of the components are known (5),

$$g_{air} = \frac{1.03 \times 1.064 \times 0.209 + 0.96 \times 0.989 \times 0.791}{1.064 \times 0.209 + 0.989 \times 0.791} = 0.98$$

while the experimental value is 1.0. There is quite a variation in the experimental data from various sources (7), and a better check cannot be expected until more experimental material is at hand.

V. AVERAGE PATH LAW FOR MIXTURES

It has been shown (3, 4) that the average path method of calculating ionization in spherical vessels holds for large values of the ratio ρ. In these former calculations the case of mixtures was not considered. It should be pointed out how the considerations presented here affect the average path method. It is only necessary to consider the gaseous mixture as a fictitious gas with properties g_m and S_m, and the average path law states

$$I_m = 3N\bar{I}\cdot\bar{x}\cdot g_m S_m \cdot \frac{P}{760}\cdot\frac{273}{273+t} \tag{15}$$

where

$$g_m \cdot S_m = \frac{\Sigma g_i S_i P_i}{P} \tag{16}$$

VI. TOTAL RELATIVE IONIZATION IN HYDROGEN–BROMINE MIXTURES

It should be of interest to make a sample calculation of the relative total ionization (g_m) for gaseous mixtures of hydrogen and bromine as a function of their partial pressures. The stopping powers of hydrogen and bromine are 0.24 and 2.80, respectively. The latter value was obtained from Glasson's rule (2). Their relative total ionizations[1] are, respectively, 1.00 and 1.35. Then

$$g_m = \frac{g_1 S_1 P_1 + g_2 S_2 P_2}{S_1 P_1 + S_2 P_2} = \frac{0.24 P_1 + 3.78 P_2}{0.24 P_1 + 2.80 P_2} \tag{17}$$

$$S_m = \frac{S_1 P_1 + S_2 P_2}{P} = \frac{0.24 P_1 + 2.80 P_2}{P} \tag{18}$$

and

$$r_m = \frac{r_0}{S_m}\cdot\frac{760}{P}\cdot\frac{273+t}{273} \tag{19}$$

[1] The value for bromine was calculated by the method of R. D. Kleeman (Proc. Roy. Soc. London **79A**, 220 (1907)).

These equations have been applied to a set of hydrogen and bromine mixtures, where $P = 760$ mm., $t = 100°C.$, and the radius of the spherical vessel is 2.153 cm. The values of g_m for these mixtures are shown in figure

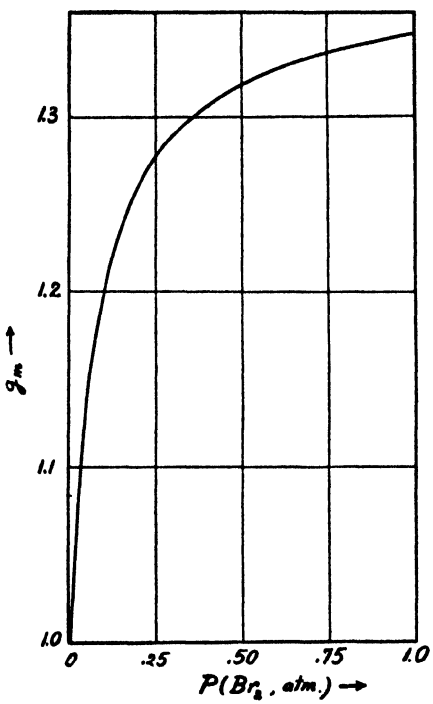

FIG. 1

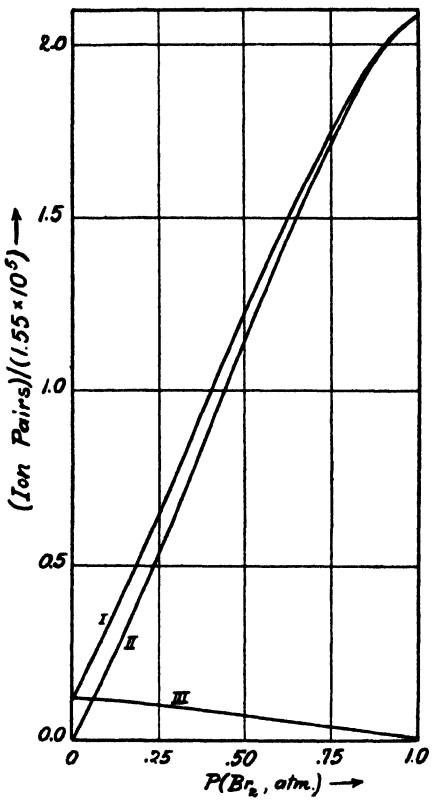

FIG. 2

FIG. 1. TOTAL RELATIVE IONIZATION OF HYDROGEN-BROMINE MIXTURES AS A FUNCTION OF THE PARTIAL PRESSURE OF BROMINE

FIG. 2. NUMBER OF ION PAIRS PER ALPHA PARTICLE AS A FUNCTION OF THE PARTIAL PRESSURE OF BROMINE

The total pressure is 1 atmosphere, the temperature is 100°C., and the radius of the spherical vessel is 2.153 cm.

I, The total number in the mixture; II, the partial ionization on bromine; III, the partial ionization on hydrogen.

1 as a function of composition. The respective total ionizations in these mixtures are shown in figure 2, where the individual ionizations falling on the hydrogen and the bromine are also shown. The method of calcula-

tion is indicated in section VII. The individual ionizations are proportional to their respective $(gSP)_i$ products, as follows from equation 2:

$$\frac{I_1}{I_2} = \frac{g_1S_1P_1}{g_2S_2P_2} \qquad \text{or} \qquad I_1 = \frac{g_1S_1P_1}{\Sigma g_iS_iP_i} \cdot I_m \tag{20}$$

VII. CALCULATION OF TOTAL IONIZATION IN HYDROGEN–BROMINE MIXTURES

The use of the foregoing results can best be illustrated by the calculation of a pertinent case. Consider a gaseous mixture of hydrogen and bromine at a total pressure of one atmosphere and partial pressures $P(H_2) = 684$ mm. and $P(Br_2) = 76$ mm. at 25°C. in a vessel of 2.153 cm. radius:

(a) The stopping power of the mixture (equation 11) is 0.50.

(b) The concordant range in the mixture is

$$r_m = \frac{3.45}{0.50} \times \frac{760}{760} \times \frac{298}{273} = 7.53 \text{ cm.} \tag{21}$$

(c) The value of $\rho = 3.5$ and $F' = 0.342$.

(d) g_m for the mixture is 1.20 (by equation 14).

(e) The total ionization in the mixture is

$$\begin{aligned} I_m &= N \times g_m \times I_T \times F' \\ &= N \times 1\ 20 \times 1\ 55 \times 10^5 \times 0.342 \\ &= N \times 0.636 \times 10^5 \end{aligned} \tag{22}$$

The average path law of Lind yields in this case the following result: $\bar{x} = 0.5833 \times 2.153 = 1.25$ cm.; $\bar{I} = 2.86 \times 10^4$ ion pair cm.$^{-1}$ (3, 4). Equation 15 yields

$$\begin{aligned} I_m &= N \times 3 \times 2.86 \times 10^4 \times 1.25 \times 1.20 \times 0.50 \times 0.984 \\ &= N \times 0.634 \times 10^5 \end{aligned} \tag{23}$$

VIII. TOTAL RELATIVE IONIZATION OF COMPOUNDS

For the purpose of calculation of g_m a compound might be considered as a mixture of its component atoms, ignoring the effect of bonding forces. This case has been adequately treated by Kleeman (footnote 1 and reference 1).

SUMMARY

The calculation for the ionization by alpha particles from radon in spherical vessels containing gaseous mixtures has been studied. The range of an alpha particle in the mixture is $r_m = P/\Sigma(P/r)_i$. The stopping power of the gas mixture is $S_m = \Sigma\ (PS)_i/P$. The total ionization relative to air (N.T.P.) is $g_m = \Sigma\ (gSP)_i/\Sigma\ (SP)_i$. The molecular ionization of the gas

mixture is given by $(gS)_m = (1/P) \Sigma (gSP)_i$. There are i components in the mixture and P is its total pressure.

It is a pleasure to thank Dr. S. C. Lind and Dr. G. B. Heisig for discussing these questions with us.

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STUDIES ON SILICIC ACID GELS. IV

THE EFFECT OF THE HYDROGEN-ION CONCENTRATION UPON THE TIME OF SET[1]

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INTRODUCTION

In a recent study in this laboratory, Hurd and Miller (5) have obtained data upon the effect of temperature on the time of set of gels of hydrated silica or silicic acid gels, as they are commonly called. The data were later examined and were found to indicate the possibility of a relation between the hydrogen-ion concentration and time of set. A further study of this possible relation has been made. The results are incorporated in this article.[2]

HISTORICAL

Numerous investigators have studied the effects of various factors upon the time of set of silicic acid gels, among such factors being the concentration of silica, the concentration of acid, salts, or foreign materials, and the temperature. The effect of the hydrogen-ion concentration has not been thoroughly studied. The effect of the acid was noted by Holmes (2) and later by Hurd and Letteron (4). The hydrogen ion specifically was noted by Glixelli and Wiertelak (1) and by Prasad and Hattiangadi (8). Ray and Ganguli (10) determined the optimum limits of pH within which setting occurred in their experiments.

To cite merely three opinions[3] concerning the setting of these gels of silicic acid, Holmes has stated that the acid molecules have a dehydrating effect upon the silicic acid, while Laskin (7) believes that certain ions in solution possess a dehydrating effect. Kröger (6) believes that the sodium ions in solution have a peptizing effect upon the silicic acid. However, from the results to be cited in this article, it seems almost certain that the peptizing action in alkaline mixtures containing silicic acid is due to the hydroxyl ion.

[1] This research was supported by a Grant-in-Aid of the National Research Council.

[2] A report was made on the first half of these results before the Colloid Division of the American Chemical Society at the meeting held in Washington, March, 1933.

[3] In the interests of economy, the bibliography has been practically omitted from this article and the article itself greatly condensed.

EXPERIMENTAL

As previously stated, Hurd and Miller have made a study of the effect of temperature upon the time of set of various mixtures of solutions of sodium silicate and acetic acid. Five commercial brands of silicate were used, known by their maker, the Philadelphia Quartz Company, as brands "S,"

TABLE 1

Time of set of sodium silicate–acetic acid mixtures at 25°C. in minutes

MIXTURE	BRAND				
	"S"	"N"	"K"	"U"	"C"
	Soda–silica ratio				
	1 3 99	1 3 33	1 2 94	1 2 52	1 2 06
	Time of set				
0	100 0	114 0	81 3	117 5	42 2
1	153 2	158 5	120 2	158 5	79 4
2	206 6	219 0	164 0	205 6	117 5
3	257 0	266 0	209 0	247 2	149 7
4	298.6	298 6	248 4	283 8	182 0
5	355 0	342 8	282.0	320 0	221 4

TABLE 2

Excess acetic acid in the mixtures whose time of set is tabulated in table 1

MIXTURE	"S"	"N"	"K"	"U"	"C"
	Soda–silica ratio				
	1 3 99	1 3 33	1 2 94	1 2 52	1 2 06
	Excess acetic acid				
0	0 177	0 237	0 185	0.242	0.127
1	0.302	0 362	0 310	0 367	0.252
2	0 427	0 487	0 435	0.492	0.377
3	0 522	0 612	0.560	0 617	0.502
4	0.677	0 737	0 685	0 742	0.627
5	0 802	0 862	0 810	0.869	0.752

"N," "K," "U," and "C."[4] Six different mixtures of each brand with acetic acid were used. Every mixture used contained the same concentration of silica, namely, 0.645 gram-mole silica per liter. From these data the time

[4] The writers wish to thank the Philadelphia Quartz Company for their kindness in supplying the silicates used in this and other research.

of set of each mixture at 25°C. was determined, the figures being given below in table 1. Also from the concentrations may be obtained what we call "excess acetic acid," namely, the difference in equivalents of the total acetic acid and the sodium of the sodium silicate, expressed as sodium hydroxide. It is thus the excess of acetic acid over that equivalent to the sodium in the sodium silicate. These data are given in table 2.

The time of set for each mixture of table 1 has been plotted as ordinate against the concentration of excess acetic acid of table 2 as abscissa. The

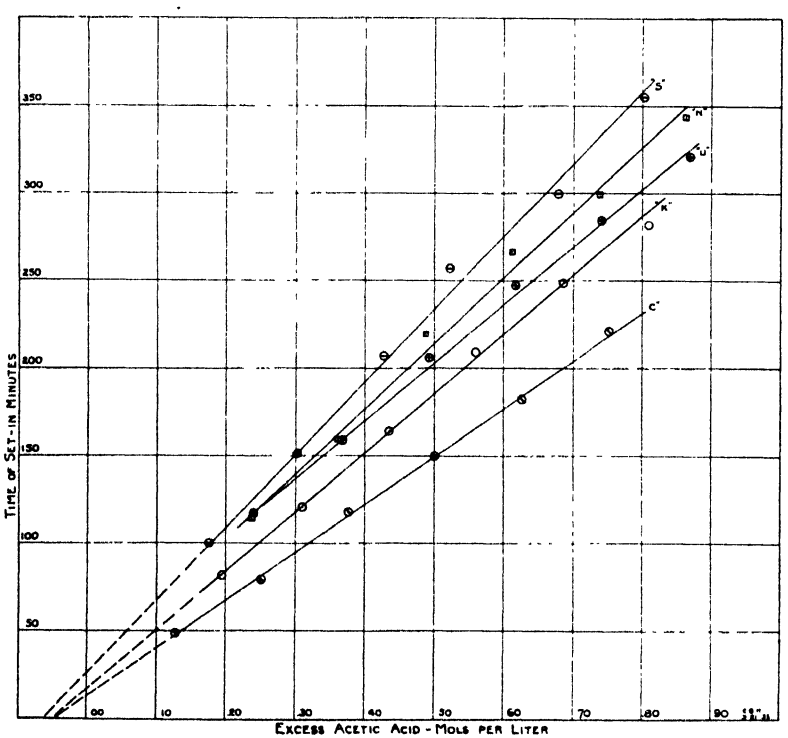

FIG. 1. TIME OF SET IN RELATION TO CONCENTRATION OF EXCESS ACETIC ACID

curve is shown in figure 1. These isothermal curves show, apparently, a linear relation between time of set and concentration of excess acid. Extrapolation to the left indicates a minimum time of set with slightly less than enough acetic acid to be equivalent to the sodium of the sodium silicate. It is well known that minimum time of set occurs in mixtures which are slightly alkaline.

This linear relation between time of set and concentration of excess acetic acid might well be taken to point toward a linear relation between the time of set and the hydrogen-ion concentration since, in solutions containing an excess of weak acid, acetic acid, in the presence of a fixed concentration of

sodium acetate, the hydrogen-ion concentration will be very nearly proportional to the acetic acid concentration.

To test the hypothesis that a linear relation exists between the time of set and the hydrogen-ion concentration, the following series of experiments were made. A series of mixtures of solutions of "E" brand sodium silicate and acetic acid were made. This silicate is particularly clear and suitable. It was used in the form of a solution, 1.23 normal with respect to sodium hydroxide. All water used in any of these solutions was distilled water which had been freshly boiled.

The mixtures were made by placing the solution of sodium silicate and the acetic acid solution in small beakers in a 23.5°C. thermostat. The amount of sodium silicate was fixed, 50 cc. of sodium silicate 1.23 normal with respect to sodium hydroxide. The relative amounts of acetic acid and water were varied, although the total volume was fixed. The silicate was poured quickly into the acid, the result mixed thoroughly by pouring back and forth several times and then divided into two 80-cc. portions. One portion was poured into a 100-cc. beaker in a 25°C. thermostat, where the time of set was determined by the tilted rod method. The other half was placed in an electrically insulated 25°C. thermostat where the pH was determined by the quinhydrone method, using a platinum wire electrode and solid quinhydrone. The whole technique for this method using quinhydrone had been carefully tested in this laboratory by an elaborate series of tests and found to be reliable.

Particular attention should be called here to the care used to keep the mixture steadily at 25°C. We have not found this mentioned elsewhere. In all cases, the rise in temperature upon mixing, due to the neutralization of sodium hydroxide by acetic acid, was measured previously. In the case just mentioned it was 1.5°C. The thermostat in which the two solutions were kept before mixing was then adjusted to that interval below 25°C., in this case, to 23.5°C.

The results of this series of experiments are given in table 3. All concentrations are in gram-moles per liter.

The relation between time of set and concentration of hydrogen ions and the logarithmic relation, namely, between logarithm of time of set and pH are shown in figure 2. Between concentrations of hydrogen ion of 1.0×10^{-6} and 7.24×10^{-5} the relation between time of set and concentration of hydrogen ion is seen to be very nearly linear. As the concentration of hydrogen ions increases, however, the time of set is seen to be slightly less than would be indicated for a linear relation. Table 3 shows, however, a large excess of acetic acid required to produce increase in the hydrogen-ion concentration.

In order to try a mixture where the hydrogen-ion concentration could be greatly increased without any appreciable increase in the amount of excess

acid, the same type of experiment was carried out using hydrochloric instead of acetic acid. Owing to the rapid change in hydrogen-ion concentration with excess hydrochloric acid, mixtures were made containing

TABLE 3

Time of set and pH data for mixtures of sodium silicate and acetic acid at 25°C.

TOTAL CH_3COOH	EXCESS CH_3COOH	pH	CONCENTRATION OF H^+	TIME OF SET	LOG TIME OF SET
				minutes	
1.363	0 975	4.14	$7\ 24 \times 10^{-5}$	331 0	2 520
1.240	0.852	4 21	6.17×10^{-5}	299 0	2 476
1.053	0.665	4.32	$4\ 79 \times 10^{-5}$	247 0	2 393
0 942	0 554	4 42	$3\ 80 \times 10^{-5}$	213 0	2 328
0 855	0 467	4 48	$3\ 31 \times 10^{-5}$	185 0	2 267
0 744	0 356	4 61	$2\ 45 \times 10^{-5}$	143 5	2 157
0 683	0 294	4 69	$2\ 04 \times 10^{-5}$	114 0	2 057
0.620	0 232	4 78	1.66×10^{-5}	97 0	1 987
0 583	0 195	4 87	$1\ 35 \times 10^{-5}$	86 0	1 935
0.558	0 170	4 92	$1\ 20 \times 10^{-5}$	74 0	1 869
0 496	0 108	5 09	$0\ 813 \times 10^{-5}$	48 5	1 686
0 459	0 071	5 29	$0\ 513 \times 10^{-5}$	33.5	1 525
0 434	0 046	5 46	$0\ 347 \times 10^{-5}$	21 5	1 332
0.422	0 034	5 60	$0\ 251 \times 10^{-5}$	16 0	1 204
0 409	0 021	5.75	0.178×10^{-5}	11 2	1 049
0.397	0 009	6 00	$0\ 100 \times 10^{-5}$	6 2	0 792

TABLE 4

Time of set and pH data for mixtures of sodium silicate and hydrochloric acid at 25°C.

pH	CONCENTRATION OF H^+	TIME OF SET	LOG TIME OF SET
		minutes	
4.21	$6\ 17 \times 10^{-5}$	75 0	1 875
4 29	5.13×10^{-5}	55 0	1 740
4.32	4.79×10^{-5}	51 0	1.708
4.35	4.47×10^{-5}	49 0	1 690
4.45	3.55×10^{-5}	40 0	1 602
4.49	3.24×10^{-5}	34 5	1 538
4.63	2.34×10^{-5}	29.5	1 470
4.82	$1\ 51 \times 10^{-5}$	21 0	1.322
4 90	$1\ 26 \times 10^{-5}$	16 5	1 217
5.03	$0\ 933 \times 10^{-5}$	14 0	1 146
5.06	0.871×10^{-5}	10.9	1 037
5.44	0.363×10^{-5}	5 5	0.740

as nearly as possible the same amount of acid with a fixed amount of silicate solutions. Checks, of course, could not be made. The excess of hydrochloric acid could not be measured, being less than 0.001. The

data are given in table 4 and plotted on figure 2. The linear relation between the time of set and the hydrogen-ion concentration is evident. In fairness, it should be pointed out here that the variation in hydrogen-ion concentration is only about twentyfold, from pH = 4.21 to 5.44. A study over a wider range is contemplated in the future.

The range with acetic acid mixtures from pH = 4.14 to pH = 6.00 represented the limits for the experiment. Higher hydrogen-ion concentrations could not be reached because of curdling of the mixture. Lower hydrogen-ion concentrations could not be reached because the mixture set too rapidly to allow accurate measurements to be made.

To investigate further the effect of the hydrogen-ion concentration upon time of set, the following series of experiments was devised. A series of

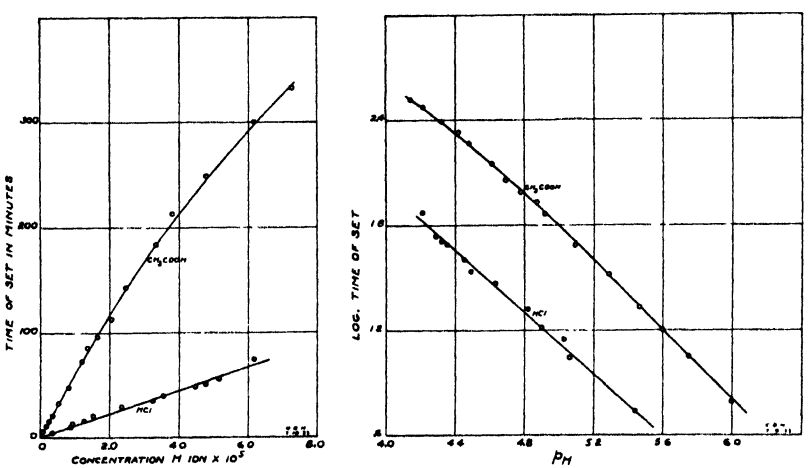

FIG. 2. RELATION BETWEEN TIME OF SET AND HYDROGEN-ION CONCENTRATION

mixtures was made in which the amount of sodium silicate ("E" brand) was fixed. The amount of acetic acid was varied, but with it was added sufficient sodium acetate so that the pH of the final mixture remained fixed. The proper quantities were determined by preliminary experiments. The proper quantities of solutions were thermostated at 23.5°C. and mixed as before. The time of set was determined with half of the mixture and the pH with the other half, each at 25°C. The solutions used were sodium silicate 1.23 normal, acetic acid 2.007 normal, and sodium acetate 2.225 molar. In all, six different series of runs were made, each at a fixed pH. The data are tabulated in table 5 and in figure 3 the time of set for each sample is plotted against the concentration of excess acetic acid.

The curves of figure 3 show that while in Series I with pH = 4.22, the time of set remains practically constant as the excess acetic acid and sodium acetate are increased, the effect of these substances is greater and greater

TABLE 5

Time of set of six series of mixtures each with a constant pH

CONCENTRATION OF EXCESS CH_3COONa	TOTAL Na	CONCENTRATION OF TOTAL CH_3COOH	CONCENTRATION OF EXCESS CH_3COOH	TIME OF SET
Series I. pH = 4.22; $H^+ = 6.03 \times 10^{-5}$				
				minutes
0 000	0 385	1 253	0 868	296
0 047	0 432	1 319	0.934	295
0 074	0 459	1.380	0 995	296
0.100	0 485	1 442	1 057	296 5
0 122	0 507	1 506	1 121	297.
Series II. pH = 4.48; $H^+ = 3.31 \times 10^{-5}$				
0 000	0 385	0 880	0 495	189
0 061	0 446	0 943	0 558	190.
0 097	0 482	1 007	0 622	190.
0 136	0 521	1 068	0 683	193
0 175	0 560	1 131	0 746	199 5
Series III. pH = 4.79; $H^+ = 1.62 \times 10^{-5}$				
0 000	0 385	0 628	0 243	101
0 101	0 486	0 691	0 306	103.
0 213	0 598	0 754	0 369	106
0 309	0 694	0 816	0.431	109 5
0 394	0 779	0 879	0 494	116.
Series IV. pH = 4.92; $H^+ = 1.20 \times 10^{-5}$				
0 000	0.385	0 565	0 180	78.
0 153	0 538	0 628	0 243	82.
0 288	0 673	0 691	0 306	87.
0 404	0.789	0 754	0 369	91
0 515	0 900	0 816	0 431	97
Series V. pH = 5.09; $H^+ = 8.13 \times 10^{-6}$				
0 000	0 385	0 502	0 117	53.
0.188	0 573	0 565	0.180	58.
0.369	0 754	0 628	0 243	64
0.543	0 928	0 691	0 306	71
0 713	1 098	0.754	0 369	77.5
Series VI. pH = 5.44; $H^+ = 3.63 \times 10^{-6}$				
0 000	0.385	0.439	0 054	24 5
0.390	0.775	0 502	0.117	31 2
0 700	1.085	0 565	0.180	39 2
1.030	1.415	0.628	0 243	45 0

All concentrations are in gram-moles per liter. Constant are NaOH, 0.385, and SiO_2, 0.645.

the higher the pH. It should also be noticed that in series I the first sample, which contains no excess sodium acetate, already contains excess acetic acid, 0.868 gram-mole per liter. In series VI, on the other hand, the first sample, which contains no excess sodium acetate, contains only 0.054 gram-mole per liter excess acetic acid. The shape of the family of curves is suggestive.

The curves and data show clearly, however, that the time of set is increased by the presence of excess acetic acid and excess sodium acetate,

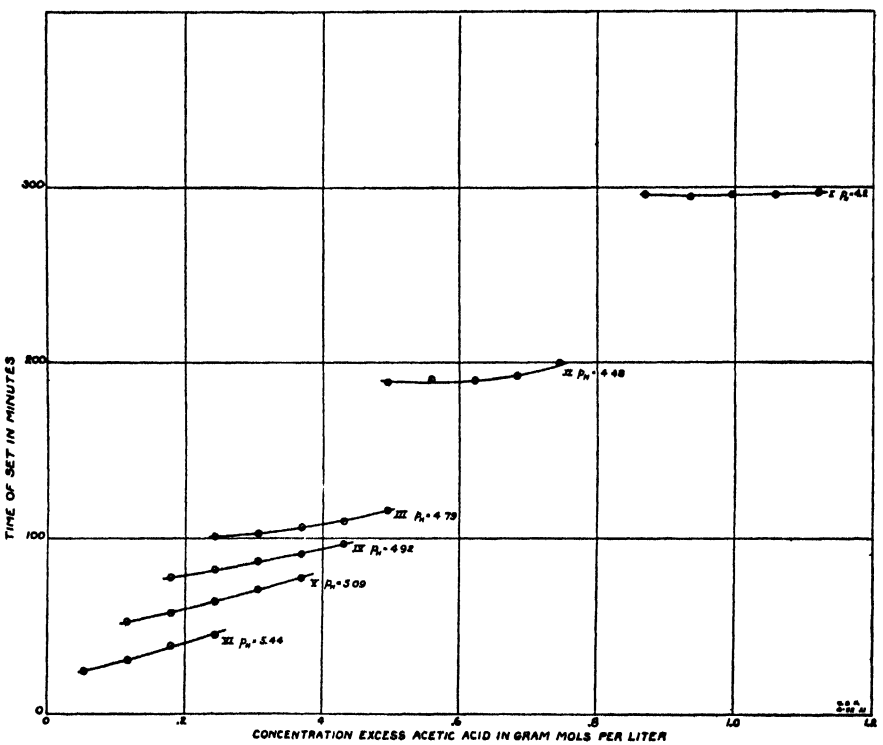

FIG. 3. TIME OF SET OF MIXTURES WITH CONSTANT pH AS A FUNCTION OF EXCESS ACETIC ACID

and is not alone a function of the hydrogen-ion concentration. We have not been able to distinguish between the effect of the sodium acetate and that of the acetic acid.

To test further the effects of sodium salts in considerable amounts upon the time of set, three series of determinations of the time of set and pH of the mixture were made, using increasing amounts of three different salts, sodium chloride, sulfate, and nitrate. The concentrations of sodium silicate and acetic acid were kept constant. The effects of electrolytes have

been studied by other investigators, especially Prasad and Hattiangadi (9). Too little attention has been paid to the simultaneous effect of variation of the pH, however, as was pointed out by Hurd and Carver (3).

The results of these three runs are given in table 6 and are plotted in figure 4. It is apparent that increasing amounts of sodium chloride show no effect upon the pH. The effect upon the time of set is marked, namely,

TABLE 6

The effect of certain sodium salts upon the time of set of silicic acid gels and upon the pH of the mixtures

SALT	CONCENTRATION	pH	TIME OF SET
			minutes
NaCl	0 000	5 09	52.5
	0 063	5.09	48.0
	0 188	5 09	40.0
	0 312	5.09	36.5
	0.468	5.09	31.3
	0 625	5.09	28.0
	0 845	5 09	25.6
	0 938	5 09	23.9
Na_2SO_4	0 000	5 09	53.0
	0 062	5 09	51 0
	0 124	5 09	48 5
	0 188	5 08	48.0
	0 250	5 08	47.5
	0 376	5 04	45 3
	0 500	5 03	44 5
	0 625	5 03	43.7
$NaNO_3$	0 000	5 09	52.5
	0 062	5 09	46.7
	0.124	5 08	43 0
	0 188	5 08	40 8
	0.250	5 08	38 8
	0.376	5 07	34.0
	0.500	5 07	31 6
	0.625	5 06	29 5

a decrease of over 50 per cent in time of set in a mixture containing approximately 1 gram-mole per liter. The sodium sulfate caused an appreciable decrease in pH, while the sodium nitrate caused a smaller decrease. Each of the pH changes should cause an increase in the time of set, estimated at about nine minutes in the case of the highest concentration of sodium sulfate. The effect of each of these three salts is to cause a marked decrease in the time of set. The sodium ion, therefore, in company with its anion,

shows no net peptizing effect, such as might be expected from the interpretations of Kröger.

The assumption may be made, therefore, in the interpretation of the data of table 5 that the sodium acetate, in addition to its function of keeping the pH constant in the presence of increasing amounts of acetic acid, would contribute materially toward decreasing the time of set. The net increase might, therefore, be due to the increasing amounts of acetic acid.

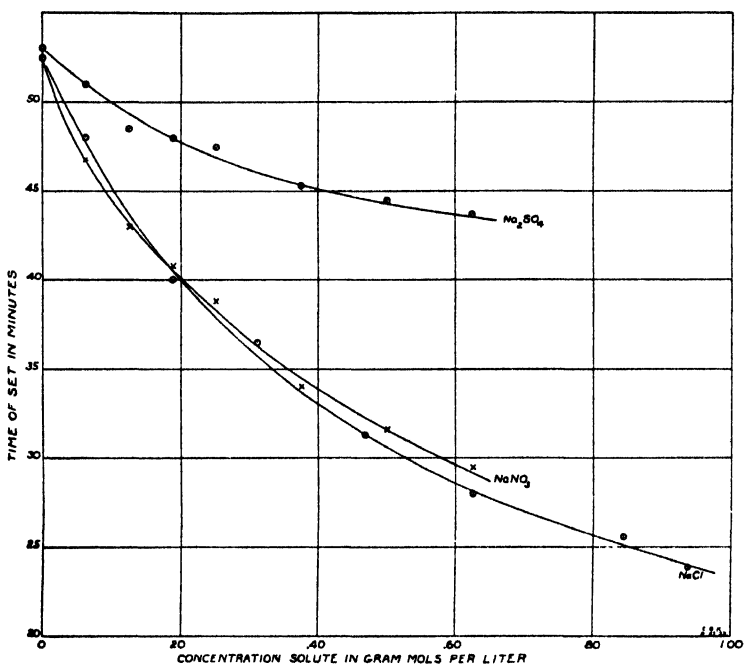

FIG. 4. EFFECT OF CERTAIN SODIUM SALTS ON TIME OF SET

DISCUSSION OF RESULTS

In this paper an attempt has been made to study so far as possible the effect, on the time of set, of the hydrogen-ion concentration, the concentration of excess acid, and of certain salts. The precautions taken to isolate these variables so far as possible have been explained. The description of details has been necessarily limited. The concentration of silica and the temperature have been kept constant throughout.

In the case of gels made from sodium silicate and acetic acid, the time of set appears to be a nearly linear function of the concentration of hydrogen ion from pH = 4.14 to 6.00. The presence of considerable excess acetic acid confuses the interpretation, however. In the case of gels made with

hydrochloric acid, the excess acid required to produce the same change in hydrogen-ion concentration is so small that it may be neglected. Here the time of set appears as a linear function of the hydrogen-ion concentration, as shown by figure 2.

We may admit the assumptions first proposed by Hurd and Letteron, namely, (1) that in dealing with the mechanism involved in the setting of a silicic acid gel we are dealing with a process which follows the laws of an ordinary chemical reaction, so far as its velocity is concerned, and (2) that for a given silica content, the time of set measures the time when a certain fixed proportion of the silica, in whatever form, in solution has reacted.

Then it may be shown easily that the specific reaction rate, k, is inversely proportional to the time of set, t'. It is not necessary that we know the order of the reaction, n. From the curve of figure 2 for the hydrochloric acid gel, the time of set appears to be not only a linear function of the hydrogen-ion concentration, but to be actually proportional to the hydrogen-ion concentration.

Since the specific reaction rate, k, is inversely proportional to the time of set, t', and since the hydroxyl-ion concentration is inversely proportional to the hydrogen-ion concentration, it would appear that the specific reaction rate, k, is proportional to the hydroxyl-ion concentration. This may suggest the idea that in silicic acid gel mixtures in this pH range, the hydroxyl ion plays the part of a catalyst.

From other work it appears, however, that in mixtures containing silicic acid of pH greater than 8, the hydroxyl ion peptizes the silica.

SUMMARY

Several series of experiments are described in which an attempt has been made to determine the effect on the time of set of silicic acid gels of the hydrogen-ion concentration and the concentrations of excess acid and of certain salts.

With gels from sodium silicate and hydrochloric acid from pH = 4.2 to 5.5, the time of set appears to be a linear function of the hydrogen-ion concentration.

With gels from sodium silicate and acetic acid from pH = 4.14 to 6.0, a nearly linear relation is evident between time of set and concentration of hydrogen ions.

With gel mixtures of constant pH, the time of set is increased by increasing amounts of acetic acid and sodium acetate.

Three salts, sodium chloride, sodium sulfate, and sodium nitrate were found to decrease the time of set considerably without causing any considerable change in the pH.

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THE REACTION OF SODIUM WITH DRY OXYGEN

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Bonnsdorff (1) stated that sodium and potassium were not oxidized by dry oxygen, and later Holt and Sims (4) published a paper on the oxidation of the alkali metals in which they announced: "Potassium and sodium (and probably lithium) are not attacked by dry oxygen and may be distilled in it without undergoing oxidation."

The truth of this statement has apparently never been questioned. Work done in this laboratory, however, has indicated that the statement is only partially correct. In the absence of moisture, sodium is coated with a film of oxide which protects it from further oxidation. In the presence of moisture, the film is unstable and, because of this fact, sodium is slowly but completely oxidized in ordinary air. The experiments upon which this belief is based will be described in detail, and it will be shown that the earlier workers either overlooked this surface film or else observed it, but failed to realize its significance.

THE EXPERIMENTS

All of the observations reported here were made upon liquid sodium–mercury amalgams. The mercury was purified by washing carefully with acid mercuric nitrate solution and then distilling under reduced pressure in a current of air. The amalgams were prepared by electrolysis of specially purified sodium chloride solutions. A platinum anode was used.

It was first observed that such amalgams could be preserved in vacuo indefinitely, but when they were stored under dry hydrogen, obtained from a cylinder in the laboratory, they behaved in an abnormal manner. If the flask holding such an amalgam was rocked, the amalgam would wet the walls and would not drain back completely. A thin mirror-like film was left adhering to the glass. The experiments reported in this paper were performed in order to explain the formation of these mirror films.

Experiment 1

A bulb was blown on the end of a glass tube and then partially filled with sodium amalgam (0.5 per cent). The bulb was then connected to a Cenco Hyvac pump and evacuated. After several minutes, the bulb and the tube were heated until the mercury was boiling freely. The tube was

then sealed off, leaving the amalgam in an evacuated bulb with a tube several inches long. A similar bulb was prepared containing pure mercury. The bulb containing the amalgam was corroded on the inside by the sodium oxide fused into the glass, but when the amalgam and the pure mercury were run into the clean tubes attached to their respective bulbs, it was not possible to distinguish between the two. Such tubes containing amalgam and mercury have been kept for three years without any visible changes.

Experiment 2

When one of the bulbs containing amalgam was sealed off and cooled, a minute crack appeared in the glass. This bulb was watched to determine the effect of the slow admission of air. Before the appearance of the crack, the amalgam could not be distinguished from mercury of the highest purity. Afterwards the amalgam became coated with a thin film which was made visible only by the wrinkles which appeared when the surface was agitated. At the same time, the amalgam acquired the property of wetting the glass to form mirrors. At first the surfaces exhibited a brilliant metallic luster, but this slowly became tarnished and dull.

Experiment 3

A bulb containing amalgam was evacuated and heated as described previously, but before sealing it off, a small amount of air was admitted. In this bulb, the surface films appeared at once. There was no tarnishing; the surfaces remained bright.

Experiment 4

Previously experiments had shown that some material present in the air caused the formation of the mirror films, and that an excess of air caused the films to tarnish. It was suspected that moisture was responsible for these effects. In order to eliminate the effect of moisture, the apparatus shown in figure 1 was constructed. Bulb C was partially filled with phosphorus pentoxide. Its capacity was approximately 35 cc. Amalgam was placed in bulb A and the apparatus was then sealed at D. The entire system was then evacuated through E and F. About 1 cc. of mercury was distilled over into B, and then all of the apparatus to the left of stopcock E was heated as uniformly as possible. Mercury distilled over into C sweeping out the last traces of air from the amalgam bulbs. The stopcocks were then closed and the apparatus was allowed to cool. The bulb C was then allowed to fill with air by opening F momentarily. The apparatus was then shaken to coat the walls of the drying chamber with the pentoxide and thereby hasten the drying process.

After 44 hours, the amalgam was transferred to bulb B. At that time, the amalgam resembled pure mercury. The dried air was then admitted to the amalgam chamber. No change could be observed until the bulbs were tilted. Then the amalgam was found to be coated with a rigid surface film, and a mirror film was left on the glass. It should be noted in particular that neither of these phenomena could have been detected if solid sodium had been exposed to dry air. The brilliance of the surface was not impaired.

Experiment 5

Experiment 4 was repeated using hydrogen from a cylinder instead of air. The gas was admitted to the amalgam after drying for 4 days. A film was formed over the surface as in the previous experiments. However, it did not appear instantly. Several seconds were required for its formation.

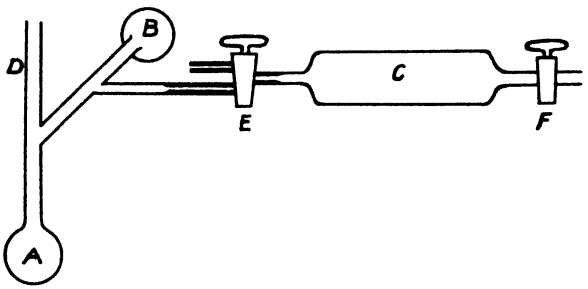

FIG. 1. APPARATUS USED TO ELIMINATE THE EFFECT OF MOISTURE

Experiment 6

The hydrogen used in the previous experiment had been obtained from an experimental plant and was suspected of containing traces of oxygen, though this has never been proved directly. Experiment 5 was repeated in duplicate using hydrogen which had been passed through freshly prepared alkaline pyrogallol solution. After intervals of 6 and 4 days, the gas was admitted to the amalgam chamber. No change could be detected. The purified hydrogen was without effect.

Experiment 7

Experiments 5 and 6 had shown that there was a small amount of the substance responsible for film formation in the hydrogen used, and that this could be removed by alkaline pyrogallol. In this experiment, carbon dioxide dried for 14 days was found to have no action upon the sodium amalgams.

Experiment 8

Nitrogen dried for 14 days over phosphorus pentoxide had no action upon a sample of sodium amalgam.

Experiment 9

Oxygen was dried for 14 days over phosphorus pentoxide, using the apparatus shown in figure 1. Before admitting the gas to the bulbs containing the amalgam, a globule of amalgam was transferred to the tube leading to the stopcock. When the oxygen was admitted, this globule was shot down the tube by the inrushing gas, leaving the tube coated with a mirror-like film, proving that the formation of the film was practically instantaneous. No change could be observed in the appearance of the amalgam in the bulbs until the apparatus was tilted. The surface crumpled like tinfoil.

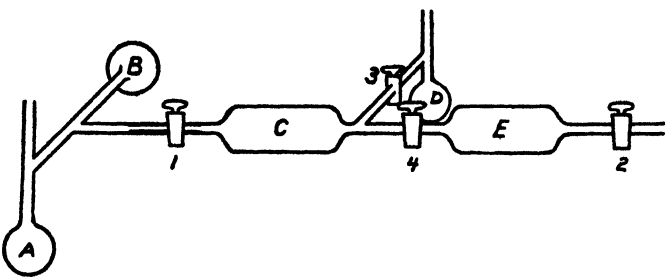

FIG. 2. APPARATUS USED TO DETERMINE THE EFFECT OF PURE WATER VAPOR UPON A SODIUM AMALGAM

Experiment 10

The apparatus shown in figure 2 was constructed in order to determine the effect of pure water vapor upon a sodium amalgam. An alkaline solution of stannous chloride was placed in bulb D and a few pieces of tin were added. It was believed that this would fix any oxygen which might remain in that bulb, and that no volatile substance except water would be introduced into the system. This bulb was then heated until the solution boiled vigorously, and then the inlet was sealed off. Bulb E was partly filled with solid sodium amalgam to remove oxygen, and liquid sodium amalgam was placed in bulb A. This compartment was boiled out as usual before closing stopcocks 1 and 2. A small amount of moisture was then admitted to the solid amalgam by opening stopcock 3. This was done to insure the absorption of oxygen from the bulbs.

After 11 days, the liquid amalgam was transferred to the clean bulb B, and stopcock 1 was opened. No change could be observed. Stopcock 4

was then closed and stopcock 3 was opened momentarily. Small lenses of water appeared almost instantly upon the surface of the amalgam, and a gas (hydrogen?) was liberated slowly until the water disappeared entirely, leaving small white flakes floating upon the surface. When more water vapor was admitted, the same cycle was repeated. The characteristic mirror formation was never in evidence, nor could any film be detected upon the surface.

Experiment 11

The apparatus shown in figure 1 was modified by providing it with two sets of amalgam bulbs, and by enlarging the drying chamber to 250-cc. capacity. Oxygen was dried in this for 49 days. The gas chamber was then connected momentarily to each of the amalgam chambers in turn. In both cases the amalgams remained bright, but the presence of a rigid film was disclosed when the apparatus was shaken. The oxygen reservoir was then connected permanently with the first amalgam chamber. After four months, there was no visible difference in the appearance of the two amalgams in contact with different amounts of oxygen.

Experiment 12

It is known that metallic sodium in air phosphoresces with a greenish light. Linneman (5) attributed this to oxidation; Reboul (7) attributed it to the reaction of sodium oxide with water vapor. More recently, Woodrow and Bowie (9) and Bowie (2) have concluded that the reaction is between metal and water vapor, and not a direct oxidation.

It was believed that if the film formation was due to a surface oxidation, and that if this oxidation gave rise to luminescence, it might be possible to detect a flash of light when the oxygen was first admitted. For this experiment, oxygen was dried for 10 days in the apparatus shown in figure 1. The oxygen was then admitted to the amalgam in a completely darkened room. There were two observers. One saw nothing, the other observed a faint flash of light in the tube leading from the stopcock to the amalgam. A small globule of amalgam had previously been transferred to this tube.

This experiment was repeated, drying the oxygen for 51 days. Two observers noticed the flash, a third did not.

This experiment was again repeated, drying the oxygen for 13 months. When the oxygen was admitted, one observer uttered an exclamation of surprise when he saw the light. He had no way of knowing the instant at which the oxygen was to be admitted.

In these experiments, no light was ever observed upon the surface of the amalgam in bulk. It was only seen in the tube where a small amount of amalgam was probably suspended in the rush of oxygen, and where the oxidation continued longer than it did on a stationary surface. It might be

added that it is not possible to estimate the actual intensity of the light because the duration of the flash is exceedingly short, and because the greater part of the walls of the tube was instantly covered with an opaque mirror film.

Experiment 13

Previous experiments had indicated that sodium amalgams react to a limited extent with dry oxygen, but no indication had been obtained as to the actual amount of oxygen involved. In order to learn more regarding the quantities involved, the apparatus shown in figure 3 was constructed. After placing phosphorus pentoxide in bulb B, the system was evacuated. It was then filled with oxygen, a stream of oxygen being forced out through

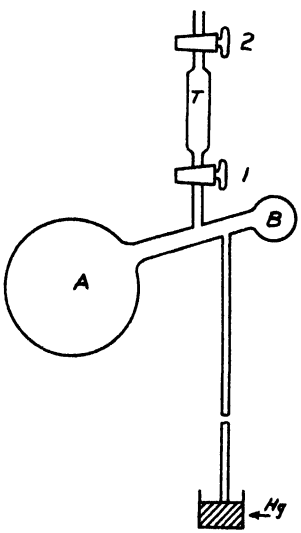

FIG. 3. APPARATUS USED TO DETERMINE THE AMOUNT OF OXYGEN INVOLVED

the manometer for about five minutes. After closing stopcock 2, the oxygen was allowed to dry for 167 days. The graduated tube T was then filled with amalgam. A small amount of gas was formed and this was removed by evacuating for 2 hours. Four hours later, 1.0 cc. of the amalgam was allowed to flow into the oxygen chamber (capacity 200 cc. ±). The amalgam was instantly covered by a rigid film. The absorption of oxygen caused less than 1 mm. change in pressure. After 24 hours, no change could be detected. An additional 2.0 cc. of amalgam was then added. After 2 days, the loss of oxygen was still too small to detect (less than 1 mm. of mercury). The apparatus was then rocked gently for 2 hours to break up the film and expose fresh surfaces to the oxygen. During that time the

pressure fell 25.0 mm., and the surface of the amalgam became coated with a heavy scum.

DISCUSSION

As a result of the experiments which have been described, it is believed that sodium is attacked by dry oxygen, and that an impervious film is formed which prevents further oxidation.

From the nature of the problem, it is always possible to argue that the gases used were not dry enough for the results to be conclusive. It is necessary, therefore, to review the original evidence for the non-reaction of dry oxygen and sodium. Bonnsdorff (1) states: "In einer vollkommen trocknen und von Kohlensäure freien Atmosphäre oxydiert sich kein Metall. Auch Kalium und Natrium bleiben in derselben ohne Oxydation." However, he admits that there is a slight oxidation for he goes on to say, "Das Kalium läuft zwar gewöhnlich in kurzer Zeit unbedeutend an, aller Wahrscheinlichkeit nach eine Folge davon, dass die Versuch nicht mit solcher Genauigkeit gemacht werden kann, dass die Wirkung des Wassers völlig ausschlossen bleibe, aber das Metall erhält sich als dann unverändert." In his experiments, the air used was dried over sulfuric acid, and it doubtless contained much more moisture than the oxygen used in our experiments. On a later page he stages that the bright metal exposed to dry air "sich unverändert mit metallischen Glanz erhielten." Our experiments proved that the presence of metallic luster was not a safe indication of the absence of a surface film.

The paper of Holt and Sims (4) is frequently quoted on the subject of the oxidation of sodium by dry oxygen. In their conclusion they state, "Potassium and sodium (and probably lithium) are not attacked by dry oxygen and may be distilled in it without undergoing oxidation." However, a study of their paper reveals that they did not actually distill these metals. They merely fused them in an atmosphere of oxygen, and heated until fumes appeared. This is analogous to the experiments of Deville (3), who reported that aluminum was absolutely resistant to oxygen even when fused.

Furthermore, Holt and Sims make the enlightening statement: "In a few experiments made by passing a stream of dried oxygen direct into molten sodium at a temperature of 235°C., no oxidation took place except at the surface, ..."

In both of these papers it is admitted that some surface oxidation took place. In both cases the authors chose to ignore this as "unbedeutend," and assumed that since the reaction did not go to completion, it would not have occurred at all if water vapor had been entirely eliminated. According to their own writings, they did not actually reach this ideal condition. Hence it still remains to be proved that oxygen can be made so dry that it will not react with sodium.

It is not possible to prove that the oxygen used in these experiments was dry, but the evidence should be considered. All gases were dried over phosphorus pentoxide, which leaves no measurable amount of water vapor in the gas (6), and the drying periods were greatly prolonged. Other investigators have used calcium chloride or sulfuric acid, which are of doubtful value. In fact, Russel (8) has reported that the amount of water left in a gas by sulfuric acid is the optimum concentration for the rapid oxidation of phosphorus.

There is the possibility that all of the water was not removed from the glass surfaces by this treatment. Even if that were the case, the partial pressure exerted by the adsorbed water must have been infinitely small and can scarcely account for the extreme speed of the initial reaction,—an action which ceased immediately, but which began again the instant that a fresh surface was exposed.

Regarding the reaction responsible for the chemiluminescence of sodium, it is evident that no light could be detected by the eye unless the reaction continued for an appreciable interval of time. Therefore the evidence in the literature favoring the reaction with water is not valid, since it does not eliminate the possibility that water is not directly responsible for the luminescence, but merely makes it possible for the oxidation to proceed slowly by preventing the formation of protective films.

CONCLUSIONS

1. It remains to be proved that oxygen can be made so dry that it will not react with sodium.

2. When sodium amalgams were exposed to oxygen dried over phosphorous pentoxide for more than a year, the amalgams were instantly covered with a protecting film which prevented further action.

3. Sodium will react with dry oxygen at room temperature with the emission of light, but the reaction ceases instantly unless water vapor is present to prevent the formation of protective films.

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THE EFFICIENCY OF ARGON AS A RADIOCHEMICAL CATALYST

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When the catalytic or sensitizing effect of inert gases on gaseous reactions produced by alpha particles from radon was first discovered by Lind and Bardwell (6), they pointed out certain puzzling facts. It appeared strange that a radiochemically inert gas such as carbon dioxide should apparently not catalyze reactions in which it is formed. Furthermore, a peculiar "depletion" effect was observed; quite generally, after the partial pressure of reactants decreased beyond the point at which half of the total ionization fell upon the catalyst, the accelerating influence of the latter diminished rapidly.

It is now known that carbon dioxide actually does speed up the carbon monoxide oxidation (8), its effect being small compared to that of krypton, helium, and nitrogen. In the original study of radiochemical sensitization, it appeared that ions formed in the sensitizing gas were completely transferred to reactants. In the carbon monoxide oxidation it was found that the dioxide is extremely inefficient as a sensitizing agent, only 14.5 per cent of its ionization being effective in promoting reaction. Because its effect was so small, carbon dioxide was at first thought to be without any influence in the radiochemical carbon monoxide oxidation. Further work (10) has disclosed that the dioxide is characteristically inefficient as a catalyst in all reactions where its influence has been studied. In the combination of hydrogen and oxygen, again about 15 per cent of the ionization falling on the carbon dioxide is transferred to reactants, while in the acetylene polymerization as much as 30 per cent seems to be utilized.

It is of interest to note that from the very start of both last mentioned reactions, more than half of the total ionization falls upon the catalyst. Accordingly we are dealing with cases which are in the range of most marked "depletion." Actually if one assumes (6) that all the carbon dioxide ionization is utilized, then the resulting velocity constants, and of course $-M/N$ ratios (molecules reacting per ion pair formed), are far below those of the normal (unsensitized) reactions, and continue to decrease further as the reactions approach completion. Referring on the other hand to the recalculated velocity constants and $-M/N$ values based on the fractional efficiency of carbon dioxide, one obtains values comparable with

those of the normal reactions, and which remain fairly constant throughout the catalyzed reaction. This is equivalent to a disappearance of the depletion effect. It thus appears possible to eliminate this puzzling feature of ionic catalysis by correcting for the proper efficiency of the ionic catalyst.

To test this possibility more fully, the existing data for reactions in which argon has been used as the inert gas have been considered more carefully from the point of view of fractional catalytic efficiency. For purposes of comparison with carbon dioxide, it is a happy coincidence that the three reactions in which the effect of the dioxide has been investigated have likewise been chosen by Lind and Bardwell (6) for a study of the argon effect.

Experimental determination of the fractional efficiency of an ionic catalyst has been fully described elsewhere (8, 10). It requires the graphical comparison of velocities of parallel reactions in spheres of the same size, containing equal quantities of radon and reactants, except that in one is found a known quantity of inert gas. Unfortunately the normal and argon catalyzed reactions were not studied under sufficiently similar conditions to permit a strict application of the method. The result is a decided downward trend in the calculated efficiency as the catalyzed reaction proceeds. However it was useful as an approximation, and in all reactions an intermediate value yielded a satisfactory fractional efficiency. Details of this preliminary work will of course be omitted. It is advisable, though, to summarize briefly the notation to be employed. Fuller descriptions are to be found in the papers already cited.

In general the velocity constant of a normal radiochemical reaction is given by

$$\left(\frac{k\mu}{\lambda}\right)' = \frac{2.303\,\Delta \log P_{\text{reactant}}}{E_0 \cdot \Delta e^{-\lambda t}}$$

where $e^{-\lambda t}$ is the initial quantity of radon in curies, and P_{reactant} is the partial pressure of reactant. For a catalyzed reaction where no correction is made for the effect of the sensitizer, the constant is denoted by $\left(\frac{k\mu}{\lambda}\right)'_c$. If the catalytic effect is considered, the corrected constant becomes

$$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}} = \frac{2.303\,\Delta \log \left[P_{\text{reactant}} + X\frac{i_{\text{catalyst}}}{i_{\text{reactant}}} P_{\text{catalyst}}\right]}{E_0 \cdot \Delta e^{-\lambda t}}$$

where $\left[X\frac{i_{\text{catalyst}}}{i_{\text{reactant}}} P_{\text{catalyst}}\right]$ is termed the ionic equivalent of the catalyst. Here, X is the fractional efficiency,[1] P_{catalyst} is the partial pressure of the

[1] The term "efficiency" as used in this paper should not be confused with the term "per cent efficiency" as used by Lind and Bardwell (6). These authors define

inert gas, and $i_{catalyst}$ and $i_{reactant}$ represent the molecular specific ionization (4) of the catalyst and reactant, respectively. The following values of specific ionization were used in this paper:

$$i_{CO} = 1.00;\ i_{CO_2} = 1.52;\ i_{H_2} = 0.24;\ i_{O_2} = 1.10;\ i_{C_2H_2} = 1.40;\ i_A = 1.245.$$

Consequently for mixtures of reacting gases we have:

$$i_{(2CO+1O_2)} = 1.03;\ i_{(2H_2+1O_2)} = 0.53$$

TABLE 1

The effect of argon on the water synthesis

$$2H_2(g) + 1O_2(g) + A(g) = 2H_2O(l) + A(g)$$

D = 1.939 cm.; E_0 = 0.0463 curie of radon; P_A = 559.5 mm.

$e^{-\lambda t}$	$P_{(2H_2+1O_2)}$	$\left(\frac{k\mu}{\lambda}\right)'_{corr}$		$-M/N$ RATIO	
		I (assuming 100 per cent efficiency)	II (assuming 40 per cent efficiency)	I* (assuming 100 per cent efficiency)	II (assuming 40 per cent efficiency)
	mm. Hg				
1 000	557 5				
0 9705	517.5	15 3	27.2	3 60	5 82
0 9174	452 5	14 3	26 1	3.21	5 59
0 8447	374 0	13 3	24 8	3 12	5 29
0 8030	332 8	12 3	24 0	2 89	5.10
0 7663	297 4	12.6	24 7	2.95	5.25
0.7069	243.7	11 9	24.4	2 80	5 17
0 6400	185 9	11 8	25 1	2 78	5 31
0.5905	147.0	11 2	24 4	2.64	5 15
0 4786	66 6	10.5	24 4	2 48	5 13
0 4158	34 9	7 8	18 8	1 82	3 93
0 3271	1 2	6.1	15.0	1 42	3 11
Average				... ...	5 30†

* These $-M/N$ ratios are calculated with the use of older values of average intensity of ionization (5). Recalculation on the basis of F as given by Glockler and Heisig (1) would yield $-M/N$ ratios lower by approximately 7 per cent.

† Pressure drop average of values down to the broken line.

The $-M/N$ ratio (i.e., molecules reacting per ion pair formed in and contributed by catalyst to reactant) is calculated from the expression:—

$$-M/N = \frac{\left(\frac{k\mu}{\lambda}\right)'_{corr.}}{F \cdot H} \frac{V}{D \cdot i_{reactant}} 1.668 \times 10^3$$

"percentage of catalytic efficiency" in a sensitized reaction as the ratio of the velocity constant obtained for a given interval (assuming complete utilization of ions formed in the catalyst, i.e., column I in tables 1, 2, and 3) over the normal velocity constant. The present author defines efficiency simply as the fraction (or per cent) of the ionization produced in the inert gas which appears to be effective in producing reaction.

where V and D are volume and diameter of the reaction sphere, H is the recoil atom correction (8), and F is the average intensity of ionization (1).

Tables 1, 2, and 3 show the influence of argon on the water synthesis, the carbon monoxide oxidation, and on the acetylene polymerization. Detailed accounts of the normal reactions as well as of the argon catalyzed water synthesis have already appeared in the literature. Only summaries of the argon catalysis of the two other reactions have been published (6). Fortunately, with Professor S. C. Lind's kind permission, the writer had access to the original experimental data collected by Lind and Bardwell, which are here presented.

From table 1 it is clear that less than 100 per cent efficiency is characteristic of argon. The $\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$ and M/N values based on this efficiency (columns I) plainly show the so-called depletion effect. On the other hand a 40 per cent efficiency (columns II) yields a satisfactory velocity constant. and $-M/N$ ratio for the whole course of the reaction, this in spite of the fact that initially 71 per cent of the total ionization falls upon the catalyst. Furthermore the reaction proceeds uniformly to the point where as much as 96 per cent of the total ionization falls upon argon. Evidently the depletion effect has been eliminated; and the average $-M/N$ ratio of 5.30 for the catalyzed reaction is in harmony with the 5.13 value for the normal synthesis (3, 6).

TABLE 2

The effect of argon on the carbon monoxide oxidation

$2CO(g) + 1O_2(g) + A(g) = 2CO_2(g) + A(g)$

D = 1.930 cm.; E_0 = 0.0418 curie of radon; P_A = 563.4 mm.

$e^{-\lambda t}$	$P_{(2CO+1O_2)}$	$\left(\frac{k\mu}{\lambda}\right)'_{\text{corr.}}$		$-M/N$ RATIO	
		I (assuming 100 per cent efficiency)	II (assuming 40 per cent efficiency)	I (assuming 100 per cent efficiency)	II (assuming 40 per cent efficiency)
	mm Hg				
1.0000	560.1				
0.9778	522.0	29.0	43.1	3.18	4.67
0 9254	444.0	26.2	40 0	2 88	4.33
0.8511	360.0	20.3	33.4	2 24	3.62
0.8076	321.0	17 5	28.6	1 94	3.10
0.7730	288.0	19.1	32.1	2.12	3.49
0 7109	243.0	15.1	25.7	1 67	2 79
0.6449	195 0	15.8	27 8	1 75	3.02
0.5983	165.6	14 2	25.6	1.58	2 77
0.4822	104.4	12.4	23 2	1.38	2.50
0.4190	74.4	11.6	22.8	1.29	2.46
0.2837	21.6	10.0	20 5	1 11	2.21

Table 2 contains a summary of the carbon monoxide oxidation. The efficiency of carbon dioxide is taken as 14.5 per cent.

Here again the assumption of a 40 per cent efficiency raises the $-M/N$ ratio. There still remains a decided downward trend which may be due to a still further diminishing efficiency of argon as reactants disappear and carbon dioxide appears. The appearance of the dioxide further complicates the system in that it contains two ionic catalysts, a type of system which is little understood. Nevertheless it is gratifying that the $-M/N$ ratio is approximately that of the normal reaction (8), which yields a value between 3 and 4.

TABLE 3

The effect of argon on the acetylene polymerization

$$xC_2H_2(g) + A(g) = (C_2H_2)_x + A(g)$$

D = 1.951 cm.; E_0 = 0.00845 curie of radon; P_A = 382 mm.

$e^{-\lambda t}$	$P_{C_2H_2}$	$\left(\frac{k\mu}{\lambda}\right)'_{corr.}$			$-M/N$ RATIO		
		I (assuming 100 per cent efficiency)	II (assuming 50 per cent efficiency)	III (assuming 60 per cent efficiency)	I (assuming 100 per cent efficiency)	II (assuming 50 per cent efficiency)	III (assuming 60 per cent efficiency
	mm Hg						
1 0000	762 6						
0 9851	733.3	212 2	256	247	17 0	20 3	19 5
0.9668	697 8	216 1	259	250	17 3	20 7	19 9
0 9489	666 2	206 0	246	236	16 6	19 7	18 9
0.9105	600.9	201.8	250	240	16 3	19 9	19 1
0 8384	489 8	203.3	256	244	16 5	20 6	19 7
0 8290	477.4	186 0	238	227	15 2	19 3	18 4
0 7945	430.9	177.4	256	242	14 5	20 8	19 6
0.6637	281.7	193 6	256	243	15 9	20 8	19 6
0.5850	211 6	178 2	254	234	14 7	20 6	19 1
0.5774	206.1	150.6	226	208	12.4	18.3	17 0
0.4886	142 9	163.4	245	223	13 5	19 8	18 1
0 4089	97.3	146.0	234	210	12 0	18 8	17 0
0.2805	45 0	119.1	201	196	9.8	16 1	14 2
0.2278	29.3	94.2	171	146	7 8	13 5	11 7
0 1371	12.3	61.0	116	99	5 0	9 1	7 9
0.0128	2.4	26 5	53	45.1	2 2	4 1	3 6
Average						20.2	18 8

A more decided example is the acetylene polymerization shown in table 3. Here it appears that argon is somewhat more efficient,[2] a value of 50 per cent or 60 per cent yielding a $-M/N$ ratio very close to the normal value. The original experiments of Lind, Bardwell, and Perry (7) sug-

[2] Compare with reference 10. Just as for argon, the efficiency of carbon dioxide in the acetylene polymerization is also greater than in the other two reactions.

gested an average $-M/N$ ratio of 19.8. A reconsideration of ionization produced, based on the Mund calculation (9) as summarized by Glockler and Heisig (1), has led Heisig to give this figure as 18. Assumption of 50 per cent efficiency (columns II) yields a constant $-M/N$ value of 20.2, while 60 per cent efficiency (columns III) gives 18.8. It is not the purpose of this discussion to determine exactly the characteristic efficiency of argon. Undoubtedly it varies somewhat with the reaction studied. The fact which does remain certain is that recalculation results in a vanishing of the depletion phenomenon. In this reaction 69 per cent of the initial ionization falls upon the reactant; and a satisfactory constant $-M/N$ ratio is obtained to a point where 78 per cent of the ionization is being carried by the catalyst.

SUMMARY

1. Existing data on the radiochemical reactions in which argon is used as an ionic catalyst have been recalculated, assuming a fractional efficiency of the catalyst. It appears that approximately 40 per cent of the ionization produced in argon is utilized in promoting the hydrogen and carbon monoxide oxidations. In the acetylene polymerization it behaves as though it possessed an efficiency of 60 per cent.

2. Satisfactory velocity constants and $-M/N$ ratios are thus obtained in regions where by far most of the total ionization is being carried by the argon.

3. It appears possible by making such a correction to eliminate the puzzling depletion effect.

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THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN CEROUS CHLORIDE SOLUTIONS AT 25°C.

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INTRODUCTION

The activity coefficient of hydrochloric acid in the alkali and alkaline earth chlorides has been determined by a number of investigators (11). Work with trivalent chlorides has been reported by Harned and Mason (4) for aluminum chloride and by Randall and Breckenridge (9) for lanthanum chloride.

In this investigation the activity coefficient of hydrochloric acid has been determined in aqueous cerous chloride solutions. The cells

$$H_2 \mid HCl(m_1),\ CeCl_3\ (m_2) \mid AgCl \mid Ag$$

containing hydrochloric acid at 0.01 molal concentration and varying amounts of cerous chloride, and hydrochloric acid and cerous chloride mixtures at constant total ionic strength have been measured at 25°C.

EXPERIMENTAL

The measurements were obtained with the usual type of H cell without the employment of vacuum technique. At the concentration of acid employed, any hydrolysis of the cerous chloride was sufficiently suppressed as to have no noticeable effect.

The cerous chloride was prepared from spectroscopically pure cerium oxalate by the method of Hönigschmidt and Holch (1, 7). The cerous chloride solutions were prepared by weight from a stock solution. This was analyzed gravimetrically for chloride as silver chloride and for cerium as CeO_2. This latter determination was carried out according to the method of Moore and Bonardi (8), except that it was found necessary, as suggested by Hillebrand and Lundell (6), to heat the oxide at 1200°C. to obtain constant weight. The two methods checked to within 1 part in 700 for the concentration of the solution.

The hydrochloric acid used was obtained by distillation of a standard arsenic-free commercial acid, discarding the first and third portions.

The silver–silver chloride electrodes used were those described by Harned (3) as type 2.

The hydrogen electrodes were prepared in the usual manner from platinum foil. The cells measured were all corrected to one atmosphere partial pressure of hydrogen (2).

All the measurements were made in a standard water thermostat at 25°C. ±0.01°C.

TABLE 1

Electromotive forces of the cells H_2 | HCl (m_1), $CeCl_3$ (m_2) | AgCl | Ag *at 25°C.*

1. Constant acid; varying salt

MOLALITY OF HCl(m_1)	MOLALITY OF $CeCl_3$(m_2)	IONIC STRENGTH μ	E	ACTIVITY COEFFICIENT γ
0 010	0.000	0.010	0 46467†	0 904*
0.010	0.005	0 04	0 44509	0 839
0.010	0.010	0 07	0 43500	0 805
0.010	0 030	0 190	0 41546	0 745
0 010	0 050	0.31	0 40535	0 717
0.010	0.075	0 46	0 39678	0 699
0.010	0 100	0.61	0 39039	0 689
0.010	0.1650	1 000	0 37991	0.662
0.010	0 250	1 51	0 36998	0 655
0.010	0 3750	2 26	0 35898	0 664
0 010	0 500	3 01	0.34908	0 698
0 010	0 750	4 51	0 33389	0 767
0 010	1 00	6 01	0 32095	0 855

2. Constant total ionic strength of 1 μ

MOLALITY OF HCl(m_1)	MOLALITY OF $CeCl_3$(m_2)	E	ACTIVITY COEFFICIENT γ (observed)	ACTIVITY COEFFICIENT γ (calculated)‡
0.100	0 1500	0.31569	0.700	0 702
0.300	0 1167	0 28113	0.727	0.727
0.500	0.0833	0 26250	0.755	0 750
0 700	0.0500	0.24904	0.779	0.776
0 900	0 0167	0.23810	0.804	0 803
1 000	0 000	0 23342	0 814	0.815

* Randall and Young (10).

† Agrees within limits of experimental error with Harned and Schupp (5) for similar cells.

‡ Equation 3.

RESULTS

The electromotive forces of the cells

$$Ag \mid AgCl \mid HCl(m_1), CeCl_3(m_2) \mid H_2 \mid HCl\ (0.01) \mid AgCl \mid Ag$$

are related to the activity coefficients and concentrations involved by the equation

$$E = 0.1183 \log \frac{\gamma}{\gamma_r} + 0.05915 \log \frac{(m_1 + 3m_2)(m_1)}{(0.01)^2} \qquad (1)$$

where γ is the activity coefficient in the salt solution and γ_r that in the reference solution of pure hydrochloric acid. m is the concentration in gram-moles per thousand grams of water. Using this equation the activity coefficients of hydrochloric acid have been calculated for the cells measured. γ_r was taken to be 0 904 for 0.01 molal hydrochloric acid (10).

Table 1 (section 1) gives results for the cells containing 0.01 molal acid and varying cerous chloride concentrations. Section 2 contains the measurements made at a constant total ionic strength of 1μ.

From the data in table 1 (section 2) we may test the equation

$$\log \gamma = \log \gamma_0 + \alpha\, m_1 \tag{2}$$

which has been shown to be valid for solutions containing hydrochloric acid in uni-univalent chloride and aluminum chloride solutions at constant total ionic strength (4, 11). γ is the activity coefficient of the acid, m_1 its molality, and γ_0 its activity coefficient in the acid-free salt solution.

A plot of log γ against m_1 at constant total ionic strength of 1 μ gave a straight line expressed by the equation

$$\log \gamma = \bar{1}.8381 + 0.0740\, m_1 \tag{3}$$

The last column of table 1 (section 2) gives the values of γ calculated from this equation. These agree, except for one concentration, to within three parts in the third decimal place of activity coefficient. This corresponds to an error of approximately 0.20 millivolt in the electromotive force of the cells.

SUMMARY

1. The activity coefficient of hydrochloric acid has been measured at 25°C. in aqueous cerous chloride solutions by means of the cell

$$H_2 \mid HCl\ (m_1),\ CeCl_3\ (m_2) \mid AgCl \mid Ag$$

2. The results at constant total ionic strength of 1μ verify the law of the linear variation of log γ and may be expressed by the equation

$$\log \gamma = \bar{1}.8381 + 0.0740\, m_1 \tag{3}$$

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PHOTOVOLTAIC CELLS CONTAINING DYE SOLUTIONS

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It has long been known (7) that when two electrodes of platinum or any other noble metal are introduced into a solution of a fluorescent dye and one of them is illuminated, a difference of potential is set up between the two electrodes, the magnitude and sign of the P.D. depending among other things on the dye, the solvent, the concentration of the dye, and the nature and intensity of the incident light.

Various theories have been advanced from time to time to explain the mechanism of this interesting phenomenon, but with apparently little success. From the similarity of the current–potential curves, obtained when an auxiliary potential is impressed on the electrodes, to analogous curves for photoelectric emission, Goldmann (4) was led to the conclusion that photovoltaic effects owed their origin to photoelectric phenomena. Subsequently van Dijck (11) obtained with a copper oxide cell evidence which is singularly at variance with such conceptions. The extensive work of Grumbach (5) has fairly well established the fact that the seat of E.M.F. is in the illuminated electrolyte and that the electrode is practically inactive. Russell (9) pictured the process as a photochemical activation of the dye molecules and the building up of the E.M.F. by the impact of the activated molecules with the electrode surface. He traced the time lag of the photopotential curves to the formation of the active molecules at some distance from the electrode, which would take a measurable time to diffuse to the electrode. Ghosh (3) developed this concept further, assumed a mutual deactivation of the molecules by collision, and by applying the Nernst equation for concentration cells derived an expression for the time rate of the rise of potential on illumination, which was verified with the experimental data of Rule (8) on fluorescein. He also showed that the maximum photopotential developed would be proportional to the square root of the intensity of the incident radiation, a prediction also proved by the data of Rule.

The concept of a photochemical origin for the E.M.F. suggests at once a close relationship between photochemical absorption and photovoltaic potential. The complete lack of data of this type has excluded a crucial examination of the hypothesis of Ghosh. The following work was started

to provide some of the required data. A point of further interest was the question of a possible parallelism between photovoltaic effects and the phenomenon of optical sensitization, so extensively employed in chromatic photography. Accordingly, erythrosin, a fluorescent dye very much used in the preparation of orthochromatic plates and a non-fluorescent dye, chrysoidine, were selected for investigation.

EXPERIMENTAL

The dyes employed were of the highest purity obtainable and were further purified by recrystallization from alcohol. A concentrated solution of the dye was first prepared by dissolving in water a weighed amount of the dye and making up the solution to a definite volume; a check on the concentration was obtained by weighing the residue on evaporating a measured volume of the solution to dryness over a water bath. The solution was preserved in the dark in stoppered bottles of resistance glass previously steamed. Under such conditions the stock solution showed no signs of deterioration and a solution of erythrosin aged in this way for four months gave results differing from a freshly made solution of the same concentration by less than 2 per cent. Solutions of desired strength were made by diluting the stock solution in the right proportion.

The dye solution was contained in a glass cell with plane parallel walls and about 4 cm. wide. A coating of non-reflecting black on the outer faces with a small rectangular patch 1.5 by 1.0 cm. on one face to admit the light served to shut off effectively stray light from the cell. The cell was mounted on a thick paraffin block.

The electrodes were rectangular pieces of platinum foil of the same size as the opening in the glass cell joined by a short length of platinum wire to sealed mercury cups. One face of the electrode and the platinum lead wire were coated with a thin film of paraffin wax, which greatly diminished local cell formation. The illuminated electrode was at a constant distance of 0.5 mm. from the glass wall and directly opposite the unpainted patch. The dark electrode almost touched the opposite wall of the cell. A light trap of a suitable shape immediately behind the illuminated electrode helped to screen efficiently the major portion of the electrolyte from the activating light.

The source of light was a transparent silica mercury burner (K.B.B. atmospheric—horizontal type) working at 85 volts and 2.0 amperes. The current in the burner was maintained constant by means of an adjustable rheostat in series. During the early experiments the entire radiation from the burner after passing through a glass cell containing cold water to filter the heat radiation was utilized for exciting the photopotentials, while, later, narrow spectral regions were isolated by interposing suitable Wratten filters of gelatin.

The cell showed a pronounced tendency to polarize; it was necessary to leave the cell a whole afternoon undisturbed when once it was polarized. The use of a potentiometer for measuring the photopotentials was thus excluded, for, during balancing, a small current is invariably drawn from the cell. A vacuum tube voltmeter was therefore considered to offer a distinct advantage; this instrument could further be made to give a continuous record of the growth of the photopotential. The principle of the valve-voltmeter is too well-known to need a full description here. It is however of interest to mention that a straight circuit utilizing a single valve operating well below its normal rated anode and filament potentials proved highly satisfactory. The arrangement was extremely stable, albeit a slight reduction in its sensitivity resulted thereby. A Philips B405 valve (normal rating,—anode 120 volts and filament 4.0 volts) was made use of with only 50 volts on the anode and 2.8 volts on the filament; the mutual conductance of the valve under these conditions was 1.0 milliampere per volt. This in conjunction with a Cambridge mirror galvanometer of sensitivity 0.33×10^{-8} ampere provided a means of measuring potentials of the order of 0.33×10^{-5} volt. The photopotentials were of the magnitude of a few millivolts. It was therefore necessary to shunt the galvanometer suitably in order to bring the potentials to be measured within the range of the instrument. Potentials of 10 millivolts and above were measured on a Cambridge microammeter with a central zero, while lower potentials could be easily measured on the mirror instrument shunted so as to give a deflection of one scale division for a grid swing of 3.3×10^{-5} volts.

It is necessary here to remark on the great stability of the arrangement. During an experiment which usually lasted some hours the creep of the zero of the instrument was ordinarily one scale division, but in inclement weather the creep at times amounted to even three divisions on the mirror galvanometer. Even this large creep meant only a change in the grid potential of a tenth of a millivolt.

The cell was connected directly between the grid and the negative end of the filament. The readings on the microammeter and the mirror galvanometer gave not only the magnitude of the photopotentials but also their sign directly.

RESULTS

The photopotentials were negative in sign in the case of erythrosin solutions, but positive with chrysoidine. It is yet early to attempt an explanation for this difference in behavior of the two dyes; possibly, the chemical constitution of the dye in addition to the solvent plays a part in determining the sign of the photo-E.M.F.

When freshly formed, the cell generally showed no P.D. between its electrodes; even in cases when the cell exhibited a minute P.D. initially, this

was never more than a fraction of a millivolt and the change of P.D. on illumination was always the same. This minute dark E.M.F. has possibly its origin in the presence of traces of impurities on the electrode surfaces.

Figure 1 illustrates the time rate of the rise of the photopotential at various concentrations of the dye; curves a, b, c, and d refer to 0.035 mg., 0.00017 mg., 0.275 mg., and 0.825 mg., respectively, of erythrosin per cubic centimeter of solution, while curves e and f refer to 0.0364 mg. and 0.0018 mg., respectively, of chrysoidine per cubic centimeter of solution. It will be noticed that the rise of E.M.F. is rapid at first, then becomes comparatively slow, and finally reaches a saturation value. This saturation P.D. is determined by the concentration of the dye and the color and intensity of the exciting light. The gradual rise of E.M.F. on illumination is in accord with the concept of diffusion of activated molecules to the electrode,

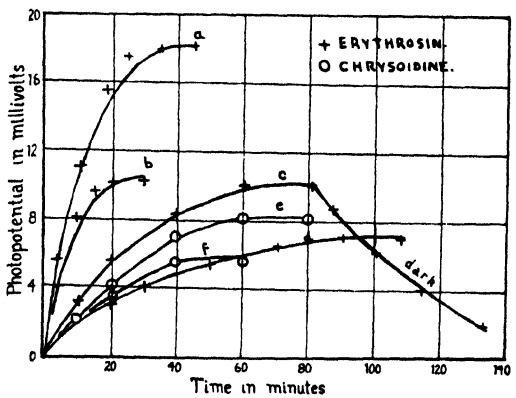

FIG. 1

a process obeying a law similar to the curves of figure 1. Again, the disappearance of the photopotential on cutting off the illumination (cf. curve c) is a much slower process than the building up. Both erythrosin and chrysoidine exhibit this behavior in all concentrations. (Only one curve has been shown for convenience.) Another interesting feature of the curves of figure 1 is that the maximum potential is reached sooner in dilute solutions. Such a behavior is also explained easily on the diffusion theory, since with a decrease in the concentration of the dye more and more of the active radiation is transmitted to the molecules contiguous to the electrode, thus reducing the diffusion path. Secondly, decreased viscosity effects at smaller concentrations of the dye may also tend to accelerate the diffusion of the activated molecules. Further evidence in support of this hypothesis was obtained in this way. By slightly altering the position of the electrode the attainment of the maximum potential could be either retarded or accelerated.

PHOTOPOTENTIAL AND CONCENTRATION OF DYE

The variation of the maximum potential with the concentration of the dye in solution is shown in curves E_1 and C_R of figure 2 for erythrosin and chrysoidine, respectively, in the composite light of the mercury arc lamp. For convenience the concentration of the dye is plotted on a logarithmic scale. Curves E_2 and E_3, giving the maximum potential developed by erythrosin solutions in the light of the mercury arc after passing through a green and yellow filter, respectively, are of some interest. While in more concentrated solutions green light is more active, in dilute solutions yellow light develops higher potentials. This difference probably arises from a difference in the extinction coefficients of the dye for the two kinds of light.

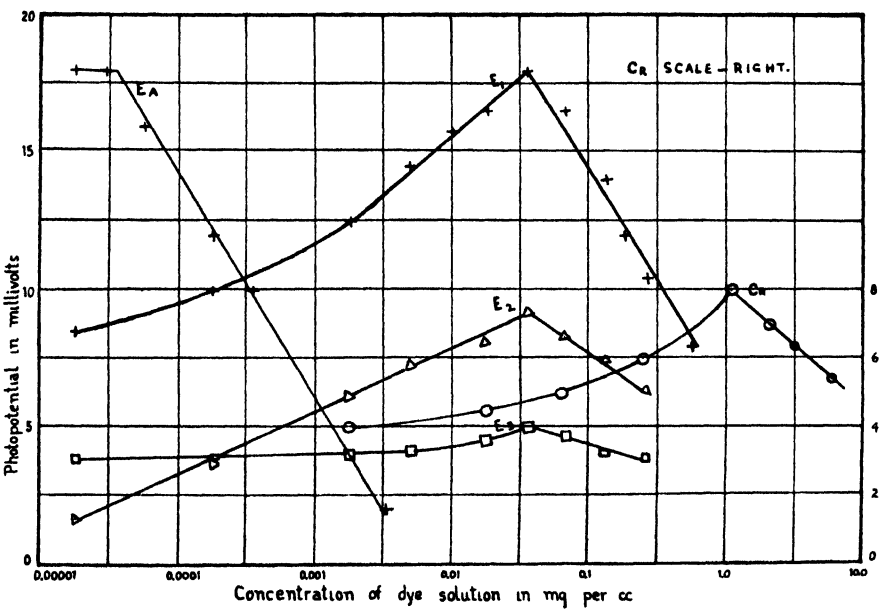

FIG. 2

Another feature of the curves E (1, 2, and 3) is that the maximum in the potential occurs at the same concentration of the dye solution irrespective of the nature of the exciting light. Still another characteristic of the curves of figure 2 (excepting E_A which will be discussed later) is that after the maximum potential has been reached, the fall of potential thereafter proceeds directly as the logarithm of the concentration of the dye solution. The same cannot be said however of the potential rise. The fall of E.M.F. with increasing concentration of the dye is most probably due to increasing absorption of the active radiation in layers immediately after the glass wall of the cell. Lowry (6) has shown by eliminating the presence of a thick absorption layer in front of the electrode that the potential–concentration

curve exhibits no maximum, but that the potential merely tends to a saturation value. Of interest in this connection are the results of some experiments in which the exciting light traversed a column 4 cm. long of the dye solution of various concentrations in a separate absorption cell before being incident on the photo-cell. The photo-cell liquid contained 0.035 mg. of the dye erythrosin per cubic centimeter of solution corresponding to the optimum concentration. Curve E_A of figure 2 depicts these results, in which the maximum photopotential developed by the photo-cell is plotted against the concentration of the absorbing liquid. E_A and the descending part of E_1 are parallel to each other, pointing to a parallelism between the two mechanisms.

PHOTOPOTENTIAL AND INTENSITY OF LIGHT

The dependence of the maximum photopotential on the intensity of the incident light was next investigated in a cell containing the optimum con-

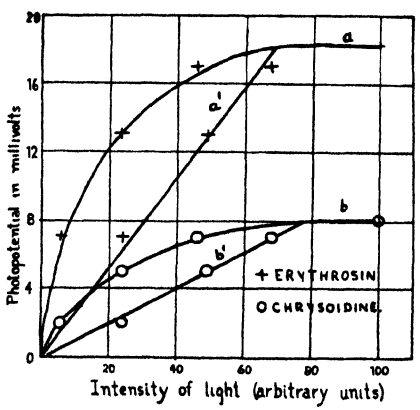

FIG. 3

centration of the dye solution. Variations in intensity of the light were produced by interposing in its path neutral tint screens of known transmission. The results are shown in figure 3. Curve a refers to erythrosine and curve b to chrysoidine. It will be noticed that with both dyes the photopotential reaches a saturation value at higher light intensities. In curves a′ and b′ the photo-E.M.F.'s are plotted as functions of the square root of the intensity. The linear course of these curves is in agreement with the deductions of Ghosh (3).

PHOTOPOTENTIAL AND WAVELENGTH OF LIGHT

The next point of interest was the location of the spectral region most active in producing the P.D. The qualitative experiments in yellow and green light recorded previously are of no use, since the transmission powers

of the filters are not known. Therefore the light from the arc was filtered through Wratten light filters; Nos. 26, 22, 12, and 35 appeared most suitable. Of these No. 26 cuts off sharply at 600$\mu\mu$ and transmits about 70 to 75 per cent of the very feeble orange lines of the mercury arc. No. 22 transmits 70 per cent of the yellow lines at 579 $\mu\mu$, while No. 12 allows to pass through 73 per cent of the green line and 75 per cent of the yellow lines. No. 35 cuts off all the ultra-violet up to 340 $\mu\mu$ and the visible beyond 460 $\mu\mu$. The transmission of this filter is about 27.5 per cent of the line at 365, 56 per cent of that at 405, and again only 27.5 per cent at 436 $\mu\mu$. This is indeed a very wide band, but sufficiently narrow to show the comparative activity of the shorter wavelengths. The results are shown in table 1.

Since the distribution of energy in the mercury arc is very different for the different wavelengths, in order to compare the activities of the various

TABLE 1

Activity of different regions of the spectrum in producing photopotentials

FILTER	PHOTOPOTENTIAL	
	Erythrosin	Chrysoidine
	mv	*mv*
No. 26	1.5	0
No. 22	9.0	1.4
No. 12	11.4	5.0
No. 35	6.0	2.0
Composite light	18 3	7 8

spectral bands it is necessary to know this energy distribution. Bensley (2) has measured this in an arc of the same type and working under similar conditions of current and voltage. He gives the following values for the energy of the different lines in the mercury arc spectrum. In addition there is present the luminous background of the arc; since this is very feeble, appreciable errors will not be introduced by neglecting it.

Energy distribution in the K.B.B. mercury arc—horizontal type, current 2 amperes, voltage 85.

Wave-length	*Energy in arbitrary units*
577–9	13
546	19
404–8	2.5
366	9

By taking into account this unequal distribution and variation of photopotential with intensity illustrated in figure 3, the transmission factors of

the Wratten filters employed, the values given in table 2 are calculated for the activity of the different regions of the spectrum in producing the photopotentials. Before discussing these values further it is advantageous to consider the absorption of the dyes. Erythrosin in water shows very slight absorption at 360$\mu\mu$ followed by strong absorption between 455 and 562$\mu\mu$ with a maximum at 518$\mu\mu$ and is transparent from 562 to 630$\mu\mu$, while chrysoidine is transparent from 330 to 360$\mu\mu$ and from 540 to 630$\mu\mu$ with a pair of unseparated bands in the region 360 to 540$\mu\mu$ (10). It is clear from a comparison of the data for photovoltaic activity with the absorption of the dye, that the maximum potential is induced by regions of the spectrum immediately following the long wavelength limit of the absorption band, both in the case of erythrosin and chrysoidine. Further, erythrosin is known to sensitize the photographic plate to wavelengths up to 600$\mu\mu$ with a pronounced maximum in the neighborhood of 580$\mu\mu$

TABLE 2

Calculated activity of different regions of the spectrum in producing photopotentials

WAVELENGTH	CALCULATED PHOTOPOTENTIAL	
	Erythrosin	Chrysoidine
	mv.	*mv.*
615$\mu\mu$	3.2	0
577–9$\mu\mu$	20 0	2.7
546$\mu\mu$	15 2	12.0
<436$\mu\mu$	10.0	4.2
Composite light	18 3	7.8

(1). The conclusion therefore seems to be reasonable that the same factors come into play both in exciting photopotentials and in optical sensitization.

SUMMARY

From a study of the photovoltaic effects in aqueous solutions of erythrosin and chrysoidine, it is shown that:

1. The usually observed maximum in the potential–concentration curve is to be attributed to the absorption of the active radiation in the column of the electrolyte in front of the electrode.
2. The photopotential varies directly as the square root of the intensity of light.
3. Wavelengths immediately following the long wave limit of the absorption band of the dye are most active in producing these potentials.

My best thanks are due to Professor H. E. Watson for continued help and guidance. The greater part of this work was carried out in the General Chemistry Department of the Indian Institute of Science, Bangalore.

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THE COMPLEXES OF MANNITOL AND SORBITOL WITH SODIUM ARSENITE AND BORAX

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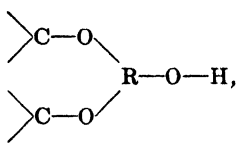
It is known that boric acid, on addition to polyhydric alcohols, enhances their optical rotation and suffers an increase in acidity (5, 8, 14, 20). These properties have been utilized for the estimation of mannitol (17), and for the titrimetric determination of boric acid (13).

van't Hoff (19) assumes in this reaction the formation of a complex having the cyclic grouping

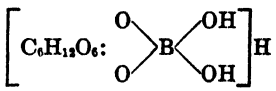


where R represents the inorganic constituent. Magnanini (15) by conductivity measurements supports the formation of a compound from one molecule of mannitol and three of boric acid, while, according to Ageno and Elena Valla (1) the ratio of mannitol to boric acid is 1:1. Fox and Gauge (9) claim to have isolated mannito-boric acid as a definite compound.

The work of Böeseken and his coworkers at Delft for the past twenty years has revealed that this property is more generally shared by a large number of polyhydroxy compounds. The ease with which these boric acid–diol complexes are formed is dependent on the positions of the hydroxyl groups, the most favored configuration being the situation of the two hydroxyl groups in the same plane and on the same side of the carbon atoms to which they are bound (4). Irvine and Steele (12) support the findings of Böeseken by a study of electrical conductivity and specific rotation of the methylated mannitols. Dubrisay (6) indicates compound formation between boric acid and mannitol, by measuring the optical rotation and surface tension of the system, as also the critical solution temperature of phenol and water in presence of the complex.

The possibility of boric acid and its salts forming more than one complex with mannitol is shown by the work of Grün and Nossowitsch (11) and by Gilmour (10) from optical rotation data. The last-mentioned author obtains a maximum rotation of 37.6° by treating sodium mannito-

borate and sodium metaborate in molecular proportions. Thus is explained the exaltation of rotation on mannitol from 22.5° (Vignon) to 28.3° (Fischer) under the influence of an excess of borax. The theory of ring structures of the boric acid complexes first suggested by van't Hoff and later adopted by Böeseken, is extended in the work of Meülenhoff (16) who ascribes to the boric acid complex of mannitol the formula



Bancroft and Davis (3), however, in a paper on "The Boric Acid Problem" doubt the compound formation between boric acid and organic hydroxy bodies, and attribute the enhanced acidity of boric acid to its increased dissociation in presence of the organic compounds dissolved therein, while the change in optical rotation is explained by "the abnormal effect of boric acid solutions."

Besides borax, sodium arsenite also induces dextrorotation (Vignon (20)), providing a method for the estimation of mannitol (2). In a solution in which the ratio of arsenious acid to mannitol is not less than 17.5, the specific rotation of the hexitol is 46.53°. From a study of the increase in solubility and neutralization values of arsenious acid in presence of mannitol, sorbitol, and other polyhydroxy compounds, Englund (7) has postulated that this acid forms with hydroxy bodies compounds similar to those formed by boric acid.

In spite of the large number of physicochemical measurements like optical rotation, electrical conductivity, hydrogen-ion concentration, solubility, and phase study, that have been applied to reveal the nature of combination of boric acid and arsenious acids with mannitol and other polyhydroxy compounds, the question remains yet unsettled. The measurement of volume changes, should they accompany the formation of these "complexes," would throw new light on the problem. The present communication relates to a dilatometric investigation of the complexes of mannitol and sorbitol with sodium arsenite and borax.

MATERIALS AND METHODS

The dilatometer devised by Sreenivasaya and Sreerangachar (18) was used in these investigations, as being best suited for the study of reactions in which the equilibrium is attained almost immediately when the reacting components are mixed. All dilatometric measurements were made at 30°C. in a thermostat. A triple shade polarimeter illuminated by a mercury arc was employed for determining the optical rotations in a 200-mm. tube at room temperature (27°C. ±1.0°C.).

d-Mannitol and *d*-sorbitol (B.D.H. products) were recrystallized from

water, samples dried at 100°C., and kept in a vacuum desiccator over phosphorus pentoxide. Solutions of these were prepared by dissolving weighed amounts of the substance in distilled water and made to volume. Arsenite solutions were prepared by boiling 198 g. of arsenious oxide with 132.5 g. of sodium carbonate, and the solution was made up to a liter (2). The strength of arsenite solution was determined iodometrically. Borax solutions saturated at 30°C. were used, the amount of dissolved borax ($Na_2B_4O_7 \cdot 10H_2O$) being estimated by acidimetric and alkalimetric titrations.

TABLE 1

Dilatometers and reaction mixtures

DILATOMETER	REACTION MIXTURE	
	Small bulb	Big bulb
Control	5 cc. of water	50 cc. of arsenite or borax solution
Experimental	5 cc. of mannitol or sorbitol solution	50 cc. of arsenite or borax solution

TABLE 2

Mannitol–arsenite

EXPERIMENT	MOLES OF ARSENITE PER GRAM-MOLE OF MANNITOL	DILATOMETRIC RISE	VOLUME INCREASE PER GRAM-MOLE OF MANNITOL	OBSERVED ROTATION $[\alpha]^{27°}_{5461}$	[M]
		cm.	*cc*		
1	0.0	—	—	—	—
2	2 4	9.1	8.05	0.26	45.88
3	4 8	12.9	10 52	0.36	63.53
4	7.2	13.8	12 14	0.39	68.84
5	9.6	14.3	12 53	0.41	72.36
6	19 2	17.3	15.22	0.49	86 48
7	24 0	17.3	15.22	0.49	86.48

The dilatometers and the reaction mixtures used were as given in table 1. As large quantities of arsenite or borax are necessary to react with a definite amount of sugar alcohol, the big bulb always received the inorganic salt solution, while the hexitol occupied the small one. The details of the experimental procedure were those followed in a previous communication (18). On mixing the solutions, one observes a depression in the control dilatometric column due to dilution of the salt solution, the order of depression depending on the strength of arsenite or borax solution used. But the experimental dilatometer treated as above records a definite rise. The equilibrium is attained within fifteen minutes, when the final readings

of the dilatometers are taken. The difference between the readings of the two dilatometers is a measure of the volume change accompanying the formation of the complex. The solutions are finally polarized. The whole operation takes one and a half hours.

TABLE 3

Mannitol-borax ($Na_2B_4O_7 \cdot 10\ H_2O$)

EXPERIMENT	MOLES OF BORAX PER GRAM-MOLE OF MANNITOL	DILATOMETRIC RISE	VOLUME INCREASE PER GRAM-MOLE OF MANNITOL	OBSERVED ROTATION $[\alpha]^{27°}_{5461}$	[M]
		cm.	*cc.*		
1	0.0	—	—	—	—
2	0.5	16.6	16.47	0.20	39.73
3	1.0	17.5	17.34	0.22	43.7
4	1.5	18.2	18.03	0.23	45.68
5	2.0	19.1	18.92	0.25	47.67
6	2.5	19.5	19.32	0.25	49.66
7	3.3	19.7	19.52	0.28	49.66
8	5.0	20.2	20 02	0.25	49.66
9	7.5	21.0	20.81	0.26	51.65
10	10 0	21.0	20.81	0.26	51.65

TABLE 4

Mannitol-arsenite

EXPERIMENT	MANNITOL	DILATOMETRIC RISE	DILATATION CONSTANT (V)	OBSERVED ROTATION $[\alpha]^{27°}_{5461}$	$[\alpha]^{27}_{D}$
	mg.	*cm.*	*cc*		
1	72.7	4.95	15.24	0.14	47.15
2	87.8	5.95	15.17	0.17	47.71
3	122.1	8.30	15.21	0.23	46.41
4	162.5	11.05	15.22	0.31	47.02
5	254.2	17.30	15.22	0.49	47.51
Mean.			15.21		47.22

RESULTS

"Complexes" of mannitol

Preliminary experiments were conducted to study the effect of adding increasing quantities of arsenite and borax to a given quantity of mannitol. Five cc. of 5 per cent mannitol and 50 cc. of arsenite or borax solutions of varying concentrations (prepared from the standard stock solutions by dilution) were used. The results are given in tables 2 and 3 and represented graphically in figure 1.

The above results show that the dilatometric change and optical rotation reach a steady maximum, beyond which further additions of arsenite or borax are no more accompanied by increases either in volume or in optical activity. To bring about this maximum change, about 19.2 moles of arsenite (see reference 2) or 7.5 moles of borax (decahydrate) per gram-mole of mannitol is found necessary. Further, this maximum corresponds to a volume increase of 15.22 cc. with arsenite and 20.81 cc. with borax per gram-mole of mannitol.

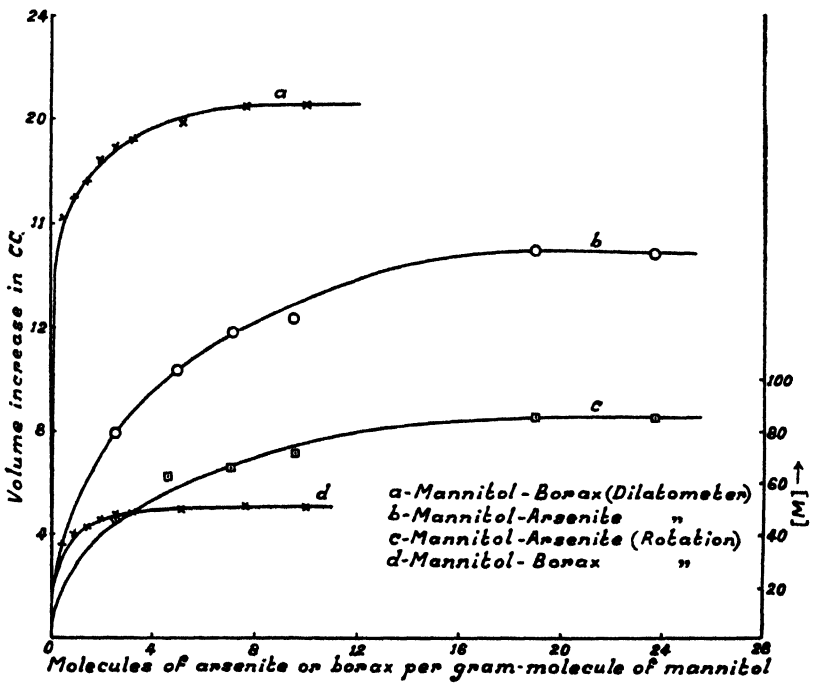


FIG. 1

The experiments were repeated with varying concentrations of the sugar alcohol and calculated amounts of arsenite and borax to induce maximum changes, and the results, incorporated in tables 4 and 5 and figure 2, confirm the above findings.

"Complexes" of sorbitol

A dilatometric study of the sorbitol–arsenite and sorbitol–borax systems has given the results embodied in table 6 and figure 2. It will be seen that the dilatation constants per gram-mole of sorbitol are 16.93 cc. and 22.38 cc. with arsenite and borax, respectively.

ACCURACY OF THE METHODS

Table 7 gives the dilatometric and polarimetric readings (taken from the previous tables) and their errors corresponding to maximum and minimum amounts of mannitol.

DISCUSSION

On mixing solutions of mannitol and sorbitol with a solution of either arsenite or borax, there occurs an appreciable increase in volume corresponding to the exaltation in optical activity (tables 2 and 3 and figure 1). This volume change observed in the case of the two hexitols is a new property found to accompany the formation of the "complexes."

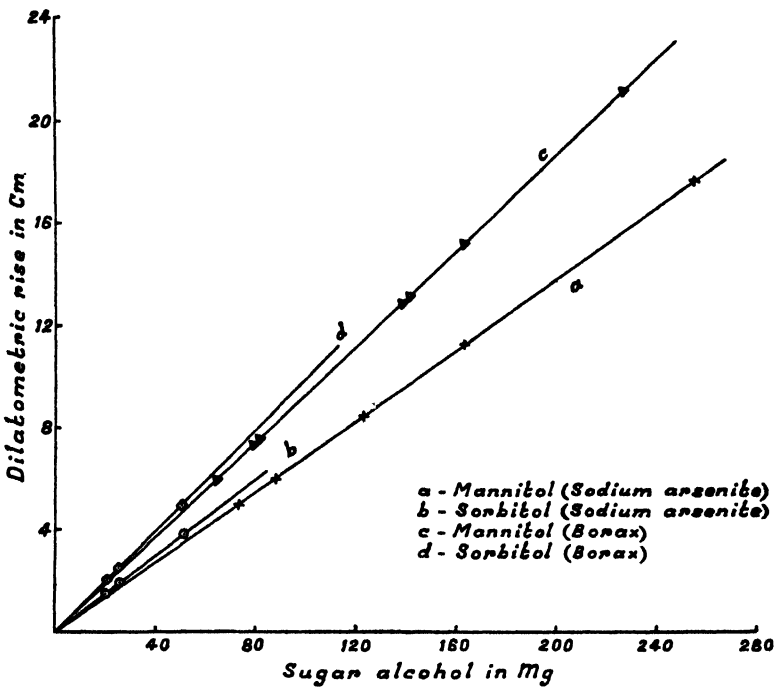


FIG. 2

A strict proportionality exists between volume change and the amounts of mannitol and sorbitol forming the complex (tables 4, 5, and 6 and figure 2).

As compared with the polarimetric estimation of mannitol or sorbitol now adopted, the dilatometric method offers a more convenient mode of determination, ensuring greater accuracy. Table 7 gives the errors in estimating mannitol in two concentrations by the two methods. It will be seen that the error in the dilatometric estimation is about 0.2 to 1 per

TABLE 5

Mannitol–borax

EXPERIMENT	MANNITOL	DILATOMETRIC RISE	DILATATION CONSTANT (V)	OBSERVED ROTATION $[\alpha]^{27°}_{54.1}$	$[\alpha]^{27°}_{D}$
	mg	*cm*	*cc*		
1	65 00	6 05	20 83	0 08	30 33
2	79 20	7 39	20 87	0 09	27 80
3	81 25	7 55	20 80	0 10	30 33
4	138 00	12 86	20 77	0 16	28 57
5	140 00	13 10	20.81	0 16	28.16
6	162 50	15 15	20 85	0 19	28 82
7	225 80	21 00	20 81	0 26	28.38
Mean			20 82		28 91

TABLE 6

Sorbitol–arsenite and sorbitol–borax

EXPERIMENT	SORBITOL	ARSENITE		BORAX	
		Dilatometric rise	Dilatation constant (V)	Dilatometric rise	Dilatation constant (V)
	mg.	*cm*	*cc*	*cm*	*cc*
1	20	1 5	16 78	2 0	22 38
2	25	1 9	17 00	2 5	22 38
3	50	3 8	17 00	5 0	22 38
Mean			16.93		22 38

TABLE 7

Accuracy of the methods

	MANNITOL	DILATOMETRIC			POLARIMETRIC		
		Reading	Error in reading	Error	Reading	Error in reading	Error
	mg	*mm.*	*mm*	*per cent*	*degrees*	*degrees*	*per cent*
Arsenite	72 7	49 5	±0 5	±1 0	0 14	±0.01	±7.0
	254 2	173 0	±0 5	0 3	0.49	±0.01	2 0
Borax	65.0	60 5	±0.5	0.8	0 08	±0 01	12.5
	225.8	210 0	±0 5	0 2	0 27	±0.01	3.7

cent, while the polarimetric method involves an error of about 2 to 12.5 per cent, which gets considerably multiplied if the test solutions happen to be colored. This limitation does not affect dilatometric estimations.

Since the volume change per gram-mole of mannitol or sorbitol is greater with borax than with arsenite, borax complexes are to be preferred for the dilatometric estimation of these sugar alcohols.

The dilatometric data obtained in this investigation strongly point to the existence of a definite compound in the systems studied. Solutions of arsenite or borax which suffer a decrease in volume on dilution with water (shown by controls) should undergo further decrease on mixing with mannitol or sorbitol solutions, if it is only a question of enhanced electrical conductivity, according to Bancroft and Davis (3). On the other hand, a definite increase in volume on mixing the two solutions has been recorded in all the experiments. Further, mannitol and sorbitol (at the concentrations used) do not register any volume change on mixing with water. Hence the dilatometric changes are more the characteristics of the formation of a new entity than the additive behavior of the preëxisting constituents. These, along with the strict proportionality found to hold between the volume increase and the amounts of hexitol reacting, point to the formation of a compound as shown by Böeseken in the course of his extensive researches.

SUMMARY

1. The formation of the "complexes" of mannitol and sorbitol with sodium arsenite and borax has been investigated in the dilatometer and also followed by polarimetric estimations in the case of mannitol.

2. The reaction is accompanied by appreciable increases of volume, which correspond to 15.21 cc. and 20.82 cc. at 30°C. per gram-mole of mannitol with arsenite and borax, respectively. The corresponding dilatation constants for sorbitol are 16.93 cc. and 22.38 cc.

3. The dilatation constants of the hexitols being higher with borax than with arsenite, borax complexes have to be preferred for the dilatometric estimation of these hexitols. It is shown that this method is more convenient and accurate than the polarimetric one now in vogue.

4. The volume expansions attending the "complex" formation and their definite relationship to the concentration of mannitol and sorbitol, suggest the formation of compounds as shown by Böeseken.

In conclusion, one of us wishes to thank the Government of Madras for the award of a scholarship that has enabled him to pursue this investigation.

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NEW BOOKS

Mass-spectra and Isotopes. By F. W. ASTON. 248 pp. New York: Longmans, Green and Co., 1933. Price: $4.80.

The present volume replaces the earlier well-known monograph of the author published by the same company under the title "Isotopes" (second edition, 1924). In expanding the title the author has sought to restrict the scope of the book somewhat, though its length has necessarily increased with the expansion of the experimental material and of its theoretical significance.

A very welcome part of the new book gives a detailed account of the construction of the new focusing mass-spectrograph and of the theory and practice of its use. The more accurate values of the relative mass of individual atoms have shown definitely the departure from the whole number rule and have established the highly important "packing fractions" for most elements and the general shape of the curve as a function of atomic mass.

As sixty-six of the possible eighty-four elements have now been subjected to isotopic analysis, the statistics have a broad significance. Only twenty simple elements have been found, and no element of odd atomic number has been found to have more than two isotopes. Two very interesting chapters on the isotopic effect in molecular and atomic spectra have been added.

As we have just entered on new and highly interesting phases of nuclear transmutation, Aston's packing fractions are an indispensable guide in the calculation of the interchange of mass and energy.

S. C. LIND.

Modern Thermodynamics by the Methods of Willard Gibbs. By E. A. GUGGENHEIM. xvi + 206 pp.; 10 figures. London: Methuen and Co., Ltd., 1933. Price: $3.50.

This book can be heartily commended to the attention of teachers and advanced students of thermodynamics. That it is not written for the beginner is evident from the fact that the author pays scant attention to the experimental basis and physical significance of the first and second laws, contenting himself with advising the reader to make himself familiar with the treatment in Planck's "Thermodynamics."

The theorems of thermodynamics are developed in a logical way, the mathematical method employed being the straightforward, analytic one. The author quite rightly criticizes the "method of cycles" on the ground that when it is simple it is usually inexact and when it is exact, it is usually complicated. The author must also be commended for employing, as Gibbs did, the illuminating term, "chemical potential," in place of the verbose expression, "the partial molal free energy." A very valuable feature of the book is the author's treatment of activities and activity coefficients. The serious student will find especially helpful the chapters on electrochemical systems, gravitational field and surface phases.

F. H. MACDOUGALL.

Fundamentals of Biochemistry in Relation to Human Physiology (Fourth Edition). By T. R. PARSONS. 12 x 18.5 cm.; 435 pp.; 26 figures. Cambridge: W. Heffer and Sons, Ltd., 1933. Baltimore: William Wood & Company, 1933. Price: $3.00.

The emphasis of this book is on *fundamentals*. In automobile parlance it is the

stripped and cut-away chassis delineating the biochemical reactions characteristic of the vital processes of the human organism.

The book is written in an extremely "human," almost conversational, style and reads as though the author were sitting across the table from you and confidentially telling you (a novice) of the wonderful chemical mechanisms operating within your body. In fulfilling this purpose the author is admirably successful. The reader needs only a minimum amount of chemical background to profit by the reading of this book. Even a good course in high school chemistry should be sufficient.

The book is thoroughly up to date and should prove of great value to the individual who wishes to acquaint himself with the essentials of animal biochemistry. It is also recommended for use in introductory courses in medical schools, for nurses, or similar groups of students.

Certain physicochemical phases of physiology are considered in chapters XVIII and XIX (pp. 327–403). Here again extremely graphic illustrations are used. For example, in speaking of hydrogen-ion concentration and bodily reactions we read "Human life as a whole is like this. Let the blood become ever so slightly acid—not even as acid as distilled water that has absorbed a trace of CO_2 from the atmosphere—and the patient dies in coma; let it become even so faintly alkaline as tap water is, and the subject goes into tetany. Between these two limits we have all our lives to try to steer a middle course." . . . . "these two extremes do not differ from each other by as much as a millionth of a gram of hydrogen ions per litre of blood!"

Each chapter has appended a list of literature citations so that the interested reader can follow up in detail such items as he wishes to pursue past the rather elementary treatment of the text.

ROSS AIKEN GORTNER.

Hydrides of Boron and Silicon. By ALFRED STOCK. 250 pp.; 36 figures. Ithaca, N. Y.: Cornell University Press, 1933. Price: $2.00.

This volume contains a portion of the subject matter of the George Fisher Baker Non-resident Lectures in Chemistry, given by Professor Stock at Cornell University in the spring of 1932. The work for the last thirty years on hydrides by Professor Stock and his coworkers is so well known that it hardly needs comment. In the present volume these excellent researches are summarized and presented in masterly fashion. Every chemist should read this volume. The ingenuity and patience shown in the execution of the experiments move one to admiration. The importance of the boron hydride problem for valency theory cannot be overestimated. This problem has special significance in the development of our ideas of chemical bonds. Main Smith has said: "These compounds of boron must be regarded as a decisive test of any theory of valency." Any theory of valency which cannot explain the structure of the hydrides of boron in a logical and self-consistent manner is doomed to failure. It is obvious then that the volume before us is one of the very important additions to the literature of chemistry.

The material is divided into thirty-two chapters. The individual hydrides are described carefully and methodically in separate sections. For cross-reference one finds complete chapters on the important reactions of these compounds. The investigator and reader desirous of looking up any certain point can find the information with the greatest ease. The apparatus used and especially developed for these researches is described fully in a special appendix. Here a warning regarding mercury poisoning is included. It is well known that Professor Stock has taken a leading position in advising research workers to use greater care in the handling of exposed mercury. The theoretical problem of the structure of these hydrides is

treated fully in four of the chapters. Literature references are given in great detail. The physical make-up of the book is excellent.

It has been a great pleasure and a privilege to the writer to have had the opportunity of reviewing this splendid treatise.

GEO. BLOCKLER.

Abridged Scientific Publications from the Kodak Research Laboratories (Volume XV, 1931–1932). Rochester, N. Y.: Eastman Kodak Company, 1933.

This volume contains complete and readily understandable summaries of sixty-one papers which have been published in a variety of journals. The subject matter of the articles varies from the description of technical procedures of interest to commercial photographers to the presentation and discussion of experimental results of importance to theoretical photochemists and physical chemists. The typography and the reproduction of illustrations are excellent.

ROBERT LIVINGSTON.

Introduction to Physical Chemistry. By ALEXANDER FINDLAY. 21 x 14 cm.; vi + 492 pp. London: Longmans, Green and Co., 1933. Price 7s. 6d.

Any book from the pen of such an experienced and competent writer as Professor Findlay is certain to have a number of outstanding qualities, and the present work is no exception. The author is of the opinion that the historical method of treatment is the one which is most sound educationally and this has been adopted successfully in the book under review; the student will read that Cailletet was an ironmaster and Joule a brewer, and these human touches should lend interest to his studies! All the subjects normally included in an introductory course of physical chemistry are discussed in an up-to-date manner: the activity concept finds frequent reference and the Lewis and Randall symbols are used in connection with the first and second laws of thermodynamics; in the brief treatment of the Nernst heat theorem, however, the German symbols have been used. A few minor errors have been noted, but the only one likely to be misleading is the statement (p. 231) that "In the ammonia equilibrium . . . . the equilibrium *constant varies* inversely as the square of the pressure." (The italics are the reviewer's.) The book, which concludes with an appendix containing some one hundred and fifty numerical problems, is worthy of consideration by all teachers of physical chemistry.

S. GLASSTONE.

Laboratory Experiments in Organic Chemistry. By ADAMS AND JOHNSON. Revised edition. xiii + 363 pp. New York: The MacMillan Company, 1933. Price: $1.90.

This is a new edition of the authors' laboratory manual, first printed in 1928. The new edition retains all of the distinctive features of the old one, and, in addition there has been considerable expansion—sixteen new experiments being included. The expansion considerably improves the book and places it in the first rank as a laboratory manual, for either the short or long courses. The list of supplementary experiments, somewhat more difficult than the average of those in the body of the text, is well selected. The printing and binding are excellent.

LEE IRVIN SMITH.

The Chemistry of Organic Compounds. By JAMES B. CONANT. x + 623 pp. New York: The MacMillan Company, 1933. Price: $4.00.

This new book by Professor Conant combines a wealth of information regarding the carbon compounds with an adequate, modern theoretical treatment. In simplicity and clarity of style the book is outstanding, and this, with the excellent choice

of material and orderly arrangement, makes the book very readable. The section on natural products is well done, and the reviewer is glad to see at last a text book of organic chemistry in which stereochemistry is treated so well. The printing and binding are splendidly done, and there are very few typographical errors. Altogether a fine piece of writing and book making.

LEE IRVIN SMITH.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. 25 x 17 cm. (a) System Nummer 8: Jod, Lieferung 2. xxiii + 245–660 pp. Price: 68.50 M (subscription price: 60 M); (b) System Nummer 59: Eisen, Teil A, Lieferung 5. xiv + 847–1166 pp. Price: 50 M (subscription price: 43.50 M). Berlin: Verlag Chemie G.m.b.H., 1933.

(a) The volume on iodine deals with hydriodic acid, the iodides of nonmetals and metals, polyhalogenides, the oxides and oxyacids of iodine, iodine fluorides, chlorides, and bromides, nitrogen iodides, and an appendix to the first part of the volume on iodine which has already appeared. In all cases the treatment is exhaustive, accurate, and critical, full numerical data, curves, and discussions of physicochemical topics being included. The literature has been very completely covered and very modern work finds its place in the treatment.

(b) The volume on iron deals with the physicochemical foundations of the technical production of malleable iron. The systems Fe–O–C, Fe–Si–O, Fe–Mn–O, Fe–P–O, Fe–S–Mn, etc., are considered. Deoxidation with manganese, carbon, silicon, aluminum, titanium and combinations of these is next dealt with. The casting of iron and steel is considered in relation to melting in crucibles, cupolas, reverberatory furnaces, Siemens-Martin furnaces, converters, and electric furnaces. The treatment of ferrous alloys includes those with manganese, chromium, molybdenum, tungsten, nickel, titanium, and vanadium. The treatment throughout is linked with technical processes and abundant references to literature are given.

The two volumes considered fully maintain the high standard of Gmelin and are unexcelled in completeness and accuracy in their field. They are very valuable contributions to the literature of chemistry.

J. R. PARTINGTON.

RESEARCHES UPON PROSPECTIVE STANDARD SUBSTANCES FOR BOMB CALORIMETRY. VI

A Study of Succinic Acid

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I. INTRODUCTION

At a recent meeting, the Commission Permanente de Thermochimie (set up by the International Union of Chemistry) has adopted the principle of a secondary standard for bomb calorimetry and requested two of their number to investigate succinic and adipic acids, both of which appeared to be worthy of consideration as prospective secondary standards.

The present paper is an answer to the Commission's request in so far as succinic acid is concerned.

II. PREPARATION OF PURE SAMPLES OF SUCCINIC ACID; MISCELLANEOUS TESTS FOR PURITY AND STABILITY; PRELIMINARY COMBUSTIONS

Succinic acid, sold by the British Drug Houses (B.D.H.) as an analytical reagent guaranteed to satisfy their special standards of purity,[1] was used as the starting material. This was first recrystallized from conductivity water at a temperature kept below 70°C., in order to avoid the risk of some slight decomposition of the acid through loss of carbon dioxide which may possibly take place at higher temperatures.[2] The crystals were filtered through a Buchner funnel and partially dried by passing a current of air through them for several hours. After standing between filter paper for two days, the acid was well crushed (in small portions at a time) in a mortar; it was then spread in thin layers in large Petri dishes and

[1] For some details, see section III, paragraph 1.

[2] According to Lamouroux (4), saturated solutions of either oxalic or malonic acids give rise to very large bubbles of carbon dioxide (with simultaneous formation of acetic acid) when heated to 68°C.; similar decompositions may possibly take place with saturated solutions of the homologues of the above acids, though this was not actually observed by Lamouroux, perhaps merely because it was not sufficiently apparent.

To get the acid quickly into solution without having to raise the temperature above 70°C., nearly four times as much water as would have been required at 100°C. was used. The solubility of succinic acid is 1 per 0.81 part of water at 100°C., and 1 per 19 parts of water at 15°C.

dried for two further periods of 6 hours (each of these being followed by careful crushing), in a desiccator containing fresh phosphoric anhydride, under a pressure reduced to approximately 0.1 mm. of mercury.

Two portions of about 4 g. each were now introduced in two weighing bottles and left to stand over phosphoric anhydride in an evacuated desiccator, the loss in weight being recorded from time to time so as to ascertain to what extent the drying had been carried out. The results given in table 1 were obtained. The loss in weight recorded during the last week, namely 0.05 to 0.08 parts per thousand, was so small that it might well be entirely accounted for by a very faint volatility of the substance when exposed to a low vacuum. But to make quite sure that if there were any water left occluded in the crystals it could only be in minute traces, the

TABLE 1

Loss in weight of succinic acid (in powder) on standing over phosphoric anhydride in vacuo

INITIAL WEIGHT	LOSS	WEIGHT AFTER 11 DAYS	LOSS	WEIGHT AFTER 8 MORE DAYS	TOTAL LOSS	LOSS IN PARTS PER THOUSAND
grams	*mg.*	*grams*	*mg*	*grams*	*mg*	
3 9407	0.9	3.9398	0.2	3 9396	1 1	0 25 per cent
3.8036	0.7	3 8029	0.3	3 8026	1 0	

TABLE 2

Isothermal heat of combustion of succinic acid, per gram weighed in vacuo, at an initial temperature of 20°C.

THE AUTHOR'S VALUES	VALUES OF VERKADE AND COOPS
3025 2, 3024.6 } 3024 9 (mean)	3026 1 { 3026.1, 3026.2, 3026 1, 3029.1 } 3026 9 (mean)

samples were dried for a further 6 hours in vacuo, at a temperature of 45°C. ± 5°C., and the heat of combustion determined directly afterwards in order to compare it with the value obtained by Verkade and Coops (8). The two groups of results are given in calories$_{15}$ in table 2, Verkade's values having previously been reduced to vacuo.

It will be seen that the author's trial values are already very near to those of Verkade and Coops, more particularly to the first three which agree exceptionally well with one another while the fourth appears to be abnormally high. If, on the other hand, it is observed that the values of the Dutch investigators (obtained by the ordinary method) seem to be usually somewhat higher than those of the author (obtained by the adiabatic method), as illustrated before in the case of salicylic acid and naphthalene (3), it

will appear that the sample of succinic acid derived in the way described from the starting material was either completely pure and dry or at least very nearly so.

Having thus satisfied himself about the apparent degree of purity of the B.D.H. preparation, by some very sensitive and independent test, the author proceeded with the preliminary examination of succinic acid from the point of view of its resistance to decomposition on heating in air or in vacuo. The stability on heating is indeed an important quality to be expected from a standard substance, as it affords a sure method to ascertain whether the drying has been carried to completion, without running the risk of deteriorating the substance. It is indeed only after such stability tests have proved satifactory that an apparently suitable substance becomes really interesting as a prospective standard and that its energy contents are shown to be worthy of a systematic study.

The stability tests now to be recorded are of two kinds: one series consists of the values obtained for the loss in weight experienced by two lots of pellets of the acid, of about 4 g. each (previously dried, when still in powder form, for four days at the ordinary temperature and then for 6 hours at a temperature in the neighborhood of 45°C.) on heating in vacuo over fresh phosphoric anhydride, to gradually increasing temperatures; the other series was obtained by determining the heat of combustion of various specimens of succinic acid after having subjected them under greatly reduced pressure to increasing temperatures. These data have been collected in tables 3 and 4.

It will be seen at once from the consideration of table 4 that the heat of combustion observed does not show any characteristic variation when the sample of succinic acid is gradually raised from the ordinary temperature to a temperature in the neighborhood of 130°C., the heating being combined with a reduction of pressure to about 0.1 mm. of mercury.

All of the results collected in tables 1, 2, and 4 prove conclusively that: (1) Succinic acid can be completely dried by heating for 6 hours in a vacuum at a temperature of 45 ±5°C. (2) The volatility of succinic acid is very small, even when it is heated in vacuo. (3) A statement recently published and according to which succinic acid, when heated in vacuo to a temperature of 55°C., would give an appreciable proportion of succinic anhydride is not justified. Indeed it can easily be calculated that the anhydrization of 1 gram of succinic acid to the extent of only 1 per cent would bring about an increase in the heat of combustion of 6.7 calories. No such change has obviously taken place during the heating; on the contrary, the mean values corresponding to the specimens which have been heated to temperatures ranging between 62°C. and 90°C. are, if anything, smaller than those corresponding to the temperature of 45°C. only.

Again, a portion of the acid (after recrystallization from conductivity

water) was dried for 7 hours under atmospheric pressure at a temperature of about 130°C. (sample A) and another portion of the same sample to

TABLE 3

Loss in weight of succinic acid (in pellet form), on heating in vacuo (in presence of phosphoric anhydride) to the various temperatures recorded

INITIAL WEIGHT OF PELLETS	LOSS IN WEIGHT OF PELLETS			TOTAL LOSS IN WEIGHT	
	3 hours at 45 ± 5°C	6 more hours at 45 ± 5°C	6 hours at 62 ± 2°C.	In milligrams	Per 10.000
grams	*mg.*	*mg*	*mg.*		
3.8853	0 2	0.5	0 4	1.1	2.5
3 5610	0.3	0 2	0 4	0 9	2 8

TABLE 4

Isothermal heat of combustion of succinic acid per gram weighed in vacuo, after heating in steps up to 130°C.

TEMPERATURE	HEATING INTERVAL	HEAT OF COMBUSTION	MEAN	SAMPLE
degrees C.	*hours*	*cal* $_{15}$		
45 ± 5	6	3025 2 3024 6	3024 9	α
45 ± 5	12	3025 6 3026 3	3025 9	β
62 ± 3	6	3023 9 3024 2	3024 2	γ
68 ± 2	4	3023 9 3023.7	3023 8	δ
70 ± 2	6	3024 3 —	3024 3	δ′
90 ± 10	2	3021 5* 3023.5	3023.5*	ε
120 ± 10	4	3025 1 —	3025.1	φ

General mean for these preliminary combustions* = 3024.6 cal.$_{15}$; mean error for mean = 0.09 part per thousand.

For the tenth of these combustions, it was observed that the bomb was slightly leaking at the end of the experiment, thus explaining the low value (3021.5); this result will consequently be neglected.

about 140°C. for a period of 6 hours (sample A_1), with the following results for the heats of combustion:

Sample	*Heat of combustion*	
A, dried at 130°C., no phosphoric anhydride	3024 8 3024 7	3024 8 (mean)
A_1, dried at 140°C., with phosphoric anhydride	3025 0 3025 4	3025 2 (mean)

However, on heating sample A for 3 hours at about 172°C., and subsequently to a still higher temperature, until the whole of the sample had melted, there was an unmistakable formation of succinic anhydride, as shown by the following values for the heat of combustion of these heated samples:

Sample	*Heat of combustion*		*Anhydride formation*
A′, heated at 172°C.	3036 0 3035 2	3035 6 (mean)	1 4 per cent
A″, heated above melting point	3094		10 per cent (approximately)

III. CONFIRMATORY COMBUSTIONS WITH SAMPLES OF SUCCINIC ACID OBTAINED BY RECRYSTALLIZATION FROM SEVERAL SOLVENTS

The results from the combustions recorded up to the present have been obtained under somewhat varying conditions (namely with different amounts of substance and cotton burnt, i.e., for a different range of temperatures than the usual one, and also in connection with a small gradual variation in the value for the water equivalent); these differences will appear clearly from the comprehensive tables (7 and 8) summarizing the whole of the calorimetric data obtained with succinic acid.

At this juncture it appeared advisable to check under more standardized conditions the results collected so far (i.e., with succinic acid obtained by recrystallization from water), and also to find out whether the substitution for water of solvents with a lower boiling point,[3] but possessing at the same time a heat of combustion per gram much larger than that of succinic acid,[4] would affect them in any way.

1. Samples recrystallized from water

The starting material for the new combustions was sample A (dried under ordinary pressure at a temperature of approximately 130°C. for 7 hours). This sample was now heated in a vacuum for a period of 7 hours at a temperature of 52 ± 2°C (without phosphoric anhydride); sample B

[3] Thus more easily got rid of and with less danger of decomposition for the substance.

[4] So that the presence of the merest trace of such solvents would quite easily reveal itself through a variation in the heat of combustion, this time however of opposite sign to that which might have been expected from the presence of traces of water.

obtained in that way was then heated in vacuo for 8 hours at a temperature of 80 ± 2°C. (in the presence of phosphoric anhydride), giving sample C; samples B and C were now burnt in duplicate directly after heating, and in the case of the latter the combustions were repeated after the pellets had stood for one month over phosphorus pentoxide (see sample C′). On the whole the results show a very good agreement amongst themselves: those obtained with samples dried in the presence of phosphoric anhydride (see samples A_1 and C) are higher by a few tenths of one calorie than those (relative to A and B) obtained in the absence of a drying agent; the difference, amounting to about 0.5 calorie in both cases, is however so small as to

TABLE 5

Isothermal heat of combustion of succinic acid, per gram weighed in vacuo, and dried for different lengths of time at the temperatures indicated

SAMPLE	DRYING TEMPERATURE	PRESSURE	DRYING AGENT	HEAT OF COMBUSTION
	degrees C	*mm.*		*cal.*$_{15}$
A	ca. 130	760		3024.8, 3024.7 — 3024.8 (mean)
A_1	ca. 140	760	P_2O_5	3025.0, 3025.4 — 3025.2 (mean)
B	52 ± 2	0.15		3024.9, 3025.5 — 3025.2 (mean)
C	80 ± 2	0.14	P_2O_5	3025.3, 3026.3 — 3025.8 (mean)
C′	Standing one month		Old P_2O_5	3025.0, 3025.9 — 3025.4 (mean)

General mean for the ten combustions = 3025.3 cal.$_{15}$ per gram in vacuo. Mean error for mean = 0.05 part per thousand.

have only little significance. The final results obtained with succinic acid recrystallized from conductivity water have been collected in table 5.

2. Recrystallization from solvents other than water

The choice of a suitable solvent for succinic acid is very limited even if no additional conditions were required, as there are in the present case. Ether was selected in spite of its small solvent power for succinic acid on account of its large heat of combustion (8805), its very low boiling point, its inertness, and also its availability in a pure state. The small sample ω_1—derived from sample C and thus completely dry—was recrystallized, from ether (A.R.) and then entirely freed from traces of solvent by heating in a vacuum (0.15 mm.) for 4 hours at a temperature of 80 ± 2°C.

Another portion of the same sample C was recrystallized from purified acetone (boiling between 55.8 and 56.0°C.) which was selected as the second solvent for practically the same reasons as those given with reference to ether, with the useful difference that the solvent power of acetone is much more suitable than that of ether with respect to succinic acid. By heating the last lot of crystals for 5 hours in vacuo at a temperature of 77 ± 2°C., a sample ω_2 was obtained. The heat of combustion found for that sample (3026.5 and 3027.1; mean = 3026.8) was however larger by 1.5 calories than the mean just recorded for the ten final combustions with the samples prepared by recrystallization from water. This small discrepancy was probably due to the presence in the sample ω_2 of a faint trace of acetone. It can be calculated indeed that, owing to the relatively large heat of combustion of acetone (7351), it would suffice that 1 g. of succinic acid would contain only 1 mg. of acetone (i.e., one part per thousand) in order to increase the heat of combustion of the contaminated sample by 1.3 calories; this is just about equal to the divergence observed. As, however, the small discrepancy might have resulted from a slight measure of purification having taken place as the consequence of the substitution of acetone for water, it was considered worth while to repeat the crystallization from acetone with a fresh sample of succinic acid. The crystals from this new recrystallization were first dried for one night over filter paper in the air, then heated for 6 hours in vacuo to a temperature of 80 ± 2°C., with alternate crushing. The value now obtained for the heat of combustion of the new sample ω_2' (3025.6 and 3026.3; mean = 3025.8) being practically identical with the general mean (3025.3) obtained previously, it was clear that the slightly too large value found for the heat of combustion of the last sample but one (from the first recrystallization with acetone) was really caused by the presence of a minute trace of acetone in the sample. As a final confirmatory test for this statement a further recrystallization of the last sample was carried out, the crystals being heated in vacuo for 5 hours at a temperature of 83 ± 2°C.; the new sample (ω_2'') was now used for a last combustion, the result of which (3025.5) was entirely in agreement with the general mean determined previously.

The results obtained for the various combustions with samples derived from recrystallizations with ether or acetone have been collected in table 6.

It can be seen that this general mean, obtained from the five combustions carried out with samples of acid recrystallized from solvents other than water, is exactly the same as that (3025.3) obtained previously when the solvent was water. The mean of means (for the whole of the twenty-six combustions carried out successfully with fifteen different samples of succinic acid) is equal to 3025.0 calories$_{15}$: it differs only by +0.4, −0.3, and −0.4 calorie from the means referring respectively to the eleven preliminary and to the ten final combustions corresponding to solvent water,

and to the five combustions corresponding to solvents ether or acetone. It can thus safely be concluded that the heat of combustion of succinic acid, per gram weighed in vacuo, and burnt isothermally at the initial temperature of 20°C. is genuinely equal to 3025 ± 1 calories$_{15}$.

IV. TECHNIQUE

1. *Apparatus*

An adiabatic calorimeter with a stirrer of the propeller type was used in conjunction with a Landrieu-Malsallez bomb (with gold lining and platinum electrodes); the jacket, of the submarine type, was heated electrolytically by means of a current of about 25 amperes (at 230 volts). The temperature rise was measured with a Beckmann thermometer having a range

TABLE 6

Isothermal heat of combustion of succinic acid per gram in vacuo, after recrystallization from ether (once) and acetone (twice)

SOLVENT	TEMPERATURE	TIME INTERVAL	HEAT OF COMBUSTION	
	degrees C.	*hours*	*cal* $_{15}$	
Ether...	80 ± 2	4	3024 9 3024.6	3024 7 (mean)
Acetone (once)	80 ± 2	6	3025 6 3026.3	3025 8 (mean)
Acetone (twice)..	83 ± 2	5	3025 5	

General mean = 3025.4 cal.$_{15}$; mean error for mean = 0.1 per thousand.

of about 5°C. (calibrated by the P.T.R. at each 0.1 division to the nearest thousandth of one degree).

2. *Method*

The "constant range method" first proposed by the author in 1926 (2) was usually adhered to. The normal range of 2°C. used in former work was again selected, starting from the same initial temperature of 19.7°C. In order to meet in advance the possible criticism that by using another range the results might be somewhat different, a larger range (2.6°C.) was used as well.

V. GENERAL INFORMATION; CALIBRATIONS; MAIN FEATURES OF THE COMBUSTIONS WITH SUCCINIC ACID

1. *General information*

In order to comply with the recommendations just adopted by the Commission Internationale Permanente de Thermochimie at a meeting

held in Paris in April, 1933, the following data have been collected hereunder:

(a) The mass of substance burnt was approximately 1.35 g. of benzoic acid and 2.80 g. of succinic acid for the range of 2°C., against 1.75 g. of benzoic acid and 3.65 g. of succinic acid for the range of 2.6°C. (b) The weight of auxiliary substance (cotton thread or wool) varied between 3 and 6 mg. (c) The mass of water introduced into the bomb was 1 g. in every case. (d) The oxygen was introduced under a constant pressure of 35 atmospheres (±5 per cent). (e) The bomb had a capacity of 450 cc. (f) The initial temperature was 19.7°C. in every instance, while the final temperature was either 21.7°C. or 22.3°C., according to whether the range selected was 2°C. or 2.6°C.

The oxygen used in connection with all the combustions reported in this paper was manufactured (in the works of the British Oxygen Company Ltd.) by fractional distillation of liquid air. As will be shown elsewhere oxygen derived from that source contains traces of combustible impurities which are exceedingly difficult to detect (owing to the extreme precision required to bring this cause of error to light in a conclusive way), so much so that they do not make their influence felt to the same extent all through the life of the oxygen cylinder. This important and curious phenomenon has been studied very closely by the author during the last three years, using several different cylinders of oxygen. Its discussion and interpretation will form the subject of a separate paper to be published shortly.

2. *Calibrations*

In order to establish once and for all for the water equivalent a fixed value of reference relative to absolutely pure oxygen,[5] a special calibration had been carried out four years ago with a sample of the preparation No. 39c of benzoic acid supplied by the Bureau of Standards, using pure oxygen (purified by slowly passing the gas over palladiumized asbestos raised to a red heat); the true constant thus obtained for the water equivalent, after reduction to an isothermal value, was 4277.1 calories$_{15}$. The data relative to that calibration have been collected in table 7, combustions 1 to 5. Since however the combustions of succinic acid were to be carried out with a newly refilled cylinder of oxygen, it was necessary either to purify this oxygen (by preheating it under suitable conditions prior to filling the bomb) or to carry out a special calibration with it. Since the former operation is very tedious and troublesome, the latter alternative was preferred. Furthermore, since the range of 2.6°C. had not been investigated before and since, on the other hand, some doubt had been expressed recently from a continental laboratory as to the true identity of successive preparations of

[5] Thus allowing one, by comparison with the value found for the water equivalent obtained with some other oxygen, to estimate the approximate purity of the latter.

TABLE 7

Water equivalent (at the temperature of 20°C.) for pressure of 35 atmospheres in the bomb and for various pressures in the cylinder of oxygen (in cal.$_{15}$ and in vacuo)

NO	WEIGHT	TEMPERATURE (CORRECTED FOR BORE)		CORRECTIONS IN TEN THOUSANDTHS			CORRECTED RISE IN °C.	CORRECTIONS IN CALORIES FOR		SAMPLE	PRESSURE	WATER EQUIVALENT (ISOTH.)	MEAN WATER EQUIVALENT
		Initial	Final	Range	Stem	Stirr		HNO_3	Cotton				
1. (1929) Calibration with preheated oxygen for *range of 2°C.* (mean error for mean = 0.11 per thousand													
1	1.3406	2.0373	4.0205	139	−5	103	1.9845	8.15	10.2	39c	—	4277.4	4277.1
2	1.3444	1.9517	3.9447	140	1	123	1.9921	—	19.4	—	—	4278.0	
3	1.3432	1.9214	3.9178	—	—	168	1.9901	8.4	15.0	—	—	4276.3	
4	1.3458	1.9135	3.9095	—	—	122	1.9953	8.6	19.0	—	—	4275.6	
5	1.3452	1.9244	3.9267	—	−1	200	1.9918	7.7	13.8	—	—	4278.0	
2. (1933) Calibration with new and non-preheated oxygen for *range of 2.6°C.*													
A. For pressure in cylinder = 116 to 113 atmospheres and 112 to 109 atmospheres. General mean (for combustions 6 to 13) = 4277.1 with mean error for mean = 0.06 per thousand													
6	1.7550	1.9031	4.4861	181	0	49	2.5962	1 8	12.6	48a	116	4276.3	4277 0
7	1.7546	1.9059	4 4908	—	—	77	2 5953	1 1	—	—	115	4276 5	
8	1.7543	1.9962	4.5810	—	—	86	2.5943	2 2	—	—	114	4277.8	
9	1.7531	1.9078	4.4935	—	—	97	2 5941	1.6	—	—	113	4277.4	
10	1.7533	1 9070	4.4909	181	0	86	2 5934	2.0	12 6	39b	112	4276 8	4277 2
11	1.7533	1.9021	4.4843	—	—	71	2.5932	1.9	—	—	111	4277.0	
12	1.7524	1.9058	4.4847	—	—	48	2 5922	1 6	—	—	110	4276.5	
13	1.7539	1.9017	4 4826	—	—	58	2 5932	1 7	—	—	109	4278.7	
B. For pressure in cylinder = 93 to 87 atmospheres. Mean error for mean = 0.09 per thousand													
14	1.7521	1.9036	4.4821	181	0	45	2.5921	1.5	15.0	39b	93	4276.7	4276 6
15	1.7530	1.8941	4.4738	—	—	38	2.5940	1.1	—	—	92	4275.6	
16	1.7487	1.9092	4.4821	180	1	48	2.5862	0.9	12 6	—	88	4277.0	
17	1.7533	1.8965	4.4766	181	0	51	2 5931	1.8	13.0	—	87	4277.3	
3. (1933) Calibration with same oxygen as in § 2, but for *range of 2.0°C.*													
A. For pressure in cylinder = 66 to 64 atmospheres. Mean error for mean = 0.08 per thousand													
18	1.3428	1.8973	3.8743	138	0	42	1 9866	1.4	7 8	39b	66	4275.1	4275 1
19	1.3413	1.8976	3.8723	—	—	44	1 9841	1.6	8.2	—	65	4275.4	
20	1.3456	1.8979	3.8798	139	—	48	1 9910	1 5	7.0	—	—	4274.2	
21	1.3466	1.8996	3.8826	—	−1	53	1 9915	1 7	6.6	—	64	4275.7	
B. For pressure in cylinder = 54 to 39 atmospheres. Mean error for mean = 0.02 per thousand													4275.2
22	1.3433	1.9028	3.8832	139	0	68	1.9875	0 7	9.2	39b	54	4275.1	4275.3
23	1.3458	1.8928	3.8763	—	—	63	1.9911	—	9.4	—	45	4275.4	
24	1.3433	1.8991	3.8784	—	−1	56	1.9875	—	—	—	39	4275.3	

General mean (for combustions 18 to 24) = 4275.2 cal.$_{15}$ with mean error for mean = 0.04 per thousand

standard benzoic acid issued by the Bureau of Standards, it was considered desirable to carry out two independent calibrations for the same range of 2.6°C., one with the preparation 39b and the other with the preparation 48a. The combustions made with the latter (see table 7, Nos. 6 to 9) gave for the water equivalent the value 4277.0, while with the former the value 4277.2 was obtained (see Nos. 10 to 13 of the same table). The mean for these eight combustions is 4277.1; it is thus identical with the value found four years earlier wth the same calorimetric system but for a range of 2°C. and with purified oxygen. This striking agreement establishes a very strong probability in favor of the purity of the oxygen used for the present research and at the same time proves that the preparations 39b, 39c, and 48a of standard benzoic acid supplied at various times by the Bureau of Standards are really identical, at least in so far as their energy contents are concerned.

But for the reason already stated that the value for the water equivalent changes appreciably as a rule when the pressure in the oxygen cylinder decreases, five more series of control calibrations were carried out for different pressures in the cylinder. Three out of these were especially carried out in connection and simultaneously with the actual combustions of succinic acid; they have for that reason been introduced in this paper (see table 7, Nos. 14 to 24). It will appear from a consideration of the last column of table 7 that in the particular case of the oxygen used for this investigation there has been a gradual decrease of some 2 calories as the pressure in the cylinder dropped from 116 to 35 atmospheres.

3. Combustions of succinic acid

Simultaneously with these calibrations, three series of combustions were carried out with succinic acid under conditions as identical as possible, in particular with respect to the two selected ranges of 2.0°C. and 2.6°C. The data relative to these experiments have been collected in table 8.

VI. GENERAL CORRECTIONS

1. Reduction to vacuo of the weights of substance burnt

(a) The density of benzoic acid was taken as equal to 1.266 (cf. International Critical Tables, Vol. I, p. 77), so that the corrective terms to be added to the weights in air (1.75 and 1.35 g.) of benzoic acid required for the two ranges of 2°C. and 2.6°C., are 1.4 and 1.1 mg., respectively.

(b) The density of succinic acid was taken as equal to 1.56 (same reference), so that the corrective terms for 3.65 and 2.80 g. of this acid are 2.3 and 1.77 mg., respectively.

(c) The weights of cotton were so small that the vacuum reduction term was quite insignificant.

TABLE 8

Isothermal heat of combustion (at constant volume) per gram of succinic acid (weighed in vacuo) at a temperature of 20°C., expressed in cal.$_{15}$

NO.	WEIGHT	TEMPERATURE (CORRECTED FOR BORE)		CORRECTIONS IN TEN THOUSANDTHS			CORRECTED RISE IN °C.	CORRECTIONS IN CALORIES FOR		SAMPLE	PRESSURE	ISOTHERMAL HEAT OF COMBUSTION	MEAN HEAT OF COMBUSTION	WATER EQUIVALENT USED
		Initial	Final	Range	Stem	Stirr		HNO_3	Cotton					
25	3.6545	1.9067	4.4826	180	1	51	2.5889	0.7	20.6	α	98	3025.2	3024.9	4276.6
26	3.6570	1.9061	4.4858	—	0	45	2.5932	14.9	19.4	—	97	3024.6		—
27	3.6595	1.9008	4.4802	—	—	42	2.5932	1.0	22.0	β	95	3025.6	3025.9	—
28	3.6591	1.9049	4.4849	—	—	45	2.5935	0.9	—	—	94	3026.3		—
29	3.6596	1.9084	4.4867	—	—	48	2.5915	0.8	20.8	γ	82	3023.9	3024.1	—
30	3.6590	1.9088	4.4861	—	—	43	2.5910	0.6	19.4	—	81	3024.2		—
31	3.6621	1.9066	4.4896	181	1	93	2.5919	1.6	14.2	δ	80	3023.9	3023.8	—
32	3.5987	1.9061	4.4398	177	0	45	2.5469	0.8	—	—	80	3023.7		—
33	3.6581	1.8970	4.4721	180	1	39	2.5893	1.2	—	δ'	78	3024.3	3024.3	—
34	3.6584	1.8918	4.4769	—	0	45	2.5886	0.7	13.4	ϵ	73	3023.5	3023.5	—
35	3.6492	1.8965	4.4657	—	—	38	2.5834	0.9	13.0	φ	72	3025.1	3025.1	—

General mean (for the eleven preliminary combustions nos. 25 to 35, range = 2.6°C.) = 3024.6 cal.$_{15}$

36	2.8058	1.9010	3.8819	138	0	66	1.9881	0.6	14.6	A	61	3024.8	3024.8	4275.2
37	2.8062	1.8998	3.8820	—	—	76	1.9884	0.4	15.0	—	60	3024.7		—
38	3.6589	1.8987	4.4756	180	—	43	2.5906	1.2	14.2	A_1	69	3025.0	3025.2	—
39	3.6565	1.8973	4.4730	—	—	45	2.5892	0.8	—	—	—	3025.4		—
40	2.8051	1.9488	3.9284	138	1	61	1.9874	0.7	13.4	B	63	3024.9	3025.2	—
41	2.8046	1.9017	3.8819	—	0	63	1.9877	0.5	14.6	—	62	3025.5		—
42	2.8070	1.9049	3.8871	—	—	68	1.9892	0.6	14.2	C	57	3025.3	3025.8	—
43	2.8036	1.9001	3.8808	—	—	70	1.9875	0.9	—	—	56	3026.3		—
44	2.8067	1.8996	3.8808	—	—	60	1.9890	0.7	15.4	C'	42	3025.0	3025.4	—
45	2.8067	1.9020	3.8827	—	—	49	1.9896	0.6	—	—	—	3025.9		—

General mean (for the ten final combustions nos. 36 to 45, usual range = 2.0°C., solvent water) = 3025.3 cal.$_{15}$. Mean error for mean = 0.05 part per thousand

46	2.8068	1.8988	3.8786	138	1	48	1.9889	0.7	15.0	ω_1	47	3024.9	3024.7	4275.2
47	2.8080	1.8986	3.8789	—	0	45	1.9896	0.6	—	—	—	3024.6		—
48	2.8063	1.8994	3.8818	—	—	72	1.9890	0.8	14.6	ω'_2	41	3025.6	3025.8	—
49	2.8054	1.9022	3.8868	—	—	94	1.9890	1.0	15.0	—	40	3026.3		—
50	2.8041	1.8987	3.8791	—	−1	65	1.9876	0.9	15.4	ω''_2	39	3025.5	3025.5	—

General mean (for the five final combustions nos. 46 to 50, range = 2.0°C., solvent ether or acetone) = 3025.4 cal.$_{15}$. Mean error for mean = 0.1 part per thousand. Mean of means (for the whole twenty-six combustions) = 3025.0 cal.$_{15}$ with mean error for mean of mean of 0.05 per thousand.

2. Reduction of the heat of combustion of succinic acid to its isothermal value

In a paper which will appear shortly elsewhere, the author has shown that, for a substance of gram-molecular weight M and heat of combustion (per gram) Q, and whose empirical formula is $C_aH_bO_cN_d$, the corrective term to be added to the value observed for the water equivalent (when determined as per international agreement by means of standard benzoic acid, whose heat of combustion is taken as 6319 calories$_{15}$ per gram) in order to give it the value which corresponds to an isothermal combustion for succinic acid is given by

$$\text{corr.}_{18} = \left(- \frac{1.7a + 7.75b + 2.5(c + d)}{M} \cdot \frac{1}{Q} - \frac{0.52}{631} \right) W \cdot \Delta t$$

where Δt represents the rise in °C. and W stands for the water equivalent in calories per degree. Hence, for succinic acid ($M = 118$; $Q = 3025$ calories per degree) whose formula is $C_4H_6O_4$, the corrective term (to be added to the water equivalent) is either $1.98 - 0.92 = 1.06$ calories per degree (for $\Delta t = 2.6$°C.) or $1.5 - 0.7 = 0.8$ calorie per degree (for $\Delta t = 2$°C.).

3. Correction for the temperature coefficient of the heat of combustion

The correction is nil in this case, since the value (6319) used for the heat combustion of benzoic acid refers to an isothermal combustion at the temperature of 20°C. and both series of combustions with either succinic acid or benzoic acid were carried out at practically the same initial temperature (19.7°C.).

4. Correction for the formation of nitric acid

For work of the highest precision it is necessary to reduce to as low a value as possible the correction for the formation of nitric acid, owing to the fact that this correction is always somewhat ill-defined. This result can be achieved by making use exclusively of nitrogen-free oxygen (or at least oxygen containing only very minute traces of nitrogen) and by sweeping the air out of the bomb prior to its filling. When, as is the case here, the volatility of the substance under investigation is very small, the same result may be obtained more easily by evacuating the bomb for a very short while under well standardized conditions.

For the actual calculation of the correction allowing for the formation of traces of nitric acid, the heat of formation of the latter under the conditions of dilution normally prevailing in the bomb was taken as equal to 230 calories per gram of acid (formed from $N + O + H_2O$).

5. Correction for the heat evolved by the combustion of the auxiliary substance used for ignition

For the present research, both cotton wool and cotton thread were used. Two auxiliary combustions were made in order to determine the heat of

combustion of the two forms of cotton used for ignition: for the wool, the heat of combustion was found to be 3954 calories per gram, while the value 3990 calories was obtained for the thread.

6. Corrections for incomplete combustion

Tests for complete combustion were carried out in a certain number of cases taken at random. The residual gases when bubbled at a very low speed through palladium chloride solution failed to indicate the presence of the merest traces of carbon monoxide.

7. Correction for the Joule effect in the ignition wire

The platinum wire used for the present work was exceedingly fine (viz., 0.03 mm. in diameter); the time required to fuse the length of wire (about 1 cm.) stretching between the two platinum electrodes was so small as to make the corrective term for the Joule effect entirely negligible.

VII. COMPARISON BETWEEN THE RESULTS OBTAINED FOR THE HEAT OF COMBUSTION OF SUCCINIC ACID BY THE AUTHOR AND OTHER OBSERVERS

Stohmann, Kleber, and Langbein (6) found for the heat of combustion of succinic acid the value 3022 calories$_{15}$, with a maximum deviation of 1.1 per thousand. This result is only smaller by about 3 calories than that of the author, the difference being remarkably small considering that the work of the German pioneers was done nearly half a century ago!

Louguinine (5) found two values, differing by 12 calories from one another, the highest of the two being still lower than that of the author by 10 calories. These results of Louguinine, like much of his work are characterized by a large maximum deviation (4.2 per thousand in his latest series of combustions with succinic acid) and have no more than a historical value!

Verkade, Hartmann, and Coops (9), on the contrary, made some trustworthy determinations—unfortunately only four in number—with two different samples of succinic acid; the general mean for their four combustions was 3026.9 calories$_{15}$, with a mean error of the mean of 0.25 per thousand and a maximum deviation from the mean of 0.75 per thousand. As already observed on page 4, the value of Verkade is higher than that found by the author by only 1.5 calories, in spite of the fact already mentioned that his fourth value (3029.1) is abnormally large and stands in sharp contrast with the three others, which are identical (3026.1). It can therefore be safely concluded that Verkade's value (3026 to 3027) is as near to that of the author (3025 $\pm$ 1) as can reasonably be expected, especially when it be remembered that the Dutch investigators used a different method (the non-adiabatic!) and worked otherwise under slightly different conditions.

More recently still, Beckers (10) found for various specimens of succinic acid values which vary between 3024.4 and 3027.4 calories$_{15}$. The final value given in the present paper (3025.0 ± 1) is thus lying well within that interval.

VIII. SUCCINIC ACID POSSESSES THE MULTIPLE QUALITIES WHICH RENDER IT SUITABLE AS A CALORIMETRIC STANDARD

The conditions which succinic acid will have to fulfill in order to be acceptable as a calorimetric standard will now be considered in turn.

1. It should be easily obtainable in an exceptionally pure state

Succinic acid will have no difficulty to establish its claim in that respect as will appear from a rapid consideration of the specifications given by the British Drug Houses for their A.R. preparation. The maximum limits of impurities allowed are: 0.05 per cent of ash (on 1 g.); 0.003 and 0.005 per cent of chlorides and sulfates, respectively (on 1 g. of acid in 20 cc. of water). Actually, the tests carried out by the author for ash, first on 1 g. and afterwards on 5 g., were entirely negative, as well as the tests for chlorides and sulfates.

It may also be recalled here that the successive recrystallizations of the original preparation, first from water and then from ether and acetone (the latter solvent being used twice), failed to show any significant variation in the value for the heat of combustion, thus giving much support to the claim of absolute purity of the substance.

2. It should be easy to dry and should remain so without requiring special precautions for keeping

It has been mentioned already that succinic acid, even when recrystallized from water, could easily be obtained in a perfectly dry condition, either by heating to a temperature of 130 to 140°C. in air or to a temperature of about 50°C. in vacuo.

The proof that succinic acid is not at all hygroscopic is given by the following results, obtained by allowing two pellets of about 1 g. to stand over night in a moist atmosphere such as that provided by a desiccator containing a dish full of water. The gain in weight was only 0.01 and 0.00 per cent for the two pellets respectively, thus giving an average gain of 0.005 per cent in 24 hours; this is just within the experimental error relative to weighings.

3. It should be perfectly stable in air, even at temperatures above 100°C., so as to allow of thorough drying

The proof that this condition is completely fulfilled by succinic acid lies in the fact that the heat of combustion of succinic acid does not change

measurably when it is heated to 140°C. (for 6 hours) under atmospheric pressure or to about 120°C. (for 4 hours) under a pressure reduced to approximately 0.1 mm. of mercury.

4. It should not be volatile

It has been found that samples of about 4 g. of succinic acid, either in the form of finely crushed powder or in pellets, lost only one part in 10.000 after being left for a fortnight in an evacuated desiccator over phosphoric anhydride.

The volatility of succinic acid, at ordinary temperature and even in vacuo, is thus exceptionally small.

5. It should be easily compressible into firm pellets

Whether the pellets of succinic acid were made after a preliminary grinding to an exceedingly fine powder or whether they were prepared directly from the larger crystals, there never arose any difficulty during the removal of the pellets from the pellet press or during subsequent manipulations. Dozens of them were seized with the forceps to and from the balance pans without any loss of material being ever measurable; some were placed in the crucible inside the bomb and oxygen admitted swiftly into the latter, without any loss of weight being experienced. In short the pellets of succinic acid behaved in all respects quite as satisfactorily as those made with benzoic acid.

6. It should be easily inflammable

The fact that some difficulty was experienced at the beginning of the first series of combustions when cotton wool was used for ignition purposes cannot be considered, in the authors' opinion, as an argument in favor of the contention that succinic acid may be somewhat deficient from the point of view of its inflammability, as has been stated about some other substances (sucrose in particular!) which possess only a small heat of combustion per gram. Indeed, succinic acid can be ignited with great ease when a suitable igniter is used, and it is not necessary to employ an unduly large quantity of igniter, since less than 4 mg. of thread was found to be always quite sufficient.

7. It must be of such a nature as will favor complete combustion

As already mentioned, all tests for carbon monoxide gave negative results; nor were deposits of unburnt carbon ever left behind.

As a corollary to the last condition, the substance should obviously not possess the tendency to project small particles of its own substance out of the crucible, before burning. The excellent agreement obtained between individual results for the heat of combustion of the acid from some thirty

combustions proves quite peremptorily that such an eventuality is not likely to arise with succinic acid

IX. CONCLUSION

Succinic acid has been shown to fulfill to a high degree all the conditions which may reasonably be required from a calorimetric standard: in particular, it has given for the heat of combustion of fifteen different samples values which show a remarkable agreement amongst themselves. Even when the values of different observers are considered, there is undoubtedly a definitely better agreement between the modern ones as there is in the case of the other prospective auxiliary standard, namely, salicylic acid: the first is markedly more stable on heating than the latter and consequently much easier to dry thoroughly and without fear of decomposition; further, the purity of succinic acid may always be tested by way of an accurate titration, which is not the case with salicylic acid.

In conclusion, the author proposes to adopt formally succinic acid as a secondary calorimetric standard for bomb calorimetry and to accept for its isothermal heat of combustion at the temperature 20°C. the value 3025 ± 1 calories_{15} (per gram weighed in vacuo).

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HIGH TEMPERATURE CATALYSTS FOR CARBON MONOXIDE OXIDATION

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The investigations of Lamb, Bray, and Frazer (20) on catalysts for the oxidation of carbon monoxide resulted in a mixed oxide catalyst, Hopcalite, which completely oxidized carbon monoxide in air at room temperature and below. Since then numerous materials have been tested by different investigators, and in most instances oxide catalysts have proved superior. Bray and Doss (7) and Almquist and Bray (2) studied copper oxide and manganese dioxide. Bone and Andrew (6) studied nickel and copper and their oxides as catalysts. Taylor and Jones (29) also investigated copper and copper oxide catalysts, while Benton (5) made a study of several oxides and mixtures. Frazer (12), Whitesell and Frazer (31), Bennett (3), and Loane (23) have shown that highly purified oxide catalysts are more active than mixtures and that the activity depends more on the purity than on promoter action.

However, all the catalysts discussed above lose their activity on heating to elevated temperatures, owing either to sintering or to a change in chemical composition. Recently some attention has been directed toward catalysts which would stand heat treatment. Engelder and Miller (10) reported tests of a number of mixed oxides, the best being a mixture of copper and titanium oxides. Engelder and Blumer (9) found that a catalyst composed of cobaltic and ferric oxides was 100 per cent efficient at room temperature and could stand heating to 890°C. without a decrease in activity. Frazer (11) and Lory (24) have investigated the metal chromites and found them to be moderately active after heating to high temperatures.

In the present investigation catalysts of the oxide type and catalysts of the chromite type were studied, and it will be convenient to discuss them under two classifications according to whether they were supported or unsupported.

The catalysts were tested by the method described by Loane (23).

UNSUPPORTED CATALYSTS

Chromites

The chromites were prepared by the ammonium chromate method which has been used in different modifications by Lazier (22), Adkins and his

coworkers (1, 8), and Lory (24). Molar weights of chromic anhydride and the metal nitrate were dissolved in water, precipitated with 3 moles of ammonium hydroxide, the precipitate filtered, washed with 250 cc. of water, and dried in an oven at 100°C. The metal ammonium chromate was decomposed by heating small portions carefully in a covered dish. The resulting chromite was heated for an hour in a crucible furnace.

Nickel chromite No. 1, copper chromite No. 1, cobalt chromite No. 1, and zinc chromite No. 1 were leached with hydrochloric acid until the excess metal oxide was dissolved out.

Cobaltites

Holgersson and his coworkers (17) report the formation of cobaltites, MCo_2O_4, when a divalent metal nitrate and cobalt nitrate in a 1:2 mole ratio are dissolved in water, evaporated, the nitrates decomposed, and the resulting mixture of oxides heated to 800–850°C. for a few hours. Natta and his coworkers (26, 27) have examined the structure of these compounds by means of the x-ray. They found them to be spinel-type compounds with a general formula $M^{++}O \cdot M_2^{+++}O_3$.

Iron cobaltite No. 2 and zinc cobaltite No. 2 were prepared by Holgersson's method. The others were prepared by dissolving the nitrates in a 2:1 mole ratio of cobalt and the other metal in water, adding a sufficient excess of ammonia to dissolve nearly all the original precipitate and form the ammonia complex (in the case of iron, naturally only the cobalt dissolved and formed the ammonia complex), evaporating the solution to dryness, decomposing the residue, and finally heating in the crucible furnace. This method gave a more finely divided, and to some extent more active, catalyst than the evaporation of the nitrates.

Ferrites

S. Hilpert (15) and Suzanne Veil (30) report the formation of ferrites by heating the mixed oxides to 900°C. Natta and Passerini (25) and Holgersson (16) have studied the crystal structure by means of x-rays and have found spinel forms.

Cobalt ferrite No. 1, copper ferrite No. 1, nickel ferrite No. 1, and manganese ferrite No. 1 were prepared by dissolving the nitrates of iron and the other metal in a 2:1 mole ratio in water, evaporating to dryness, decomposing the nitrates by heating, and finally heating the mixed oxides to the desired temperature. The ferrites No. 2 were prepared by precipitating the hydroxides from a solution of the nitrates or chlorides in a 2:1 mole ratio. The resulting hydroxides were filtered, washed with hot water, dried, and heated in the crucible furnace. Cobalt ferrite No. 2-B was washed with hot water after the final heating until the filtrate showed no test for chlorides, then heated again to 975°C.

Manganites

Cobalt manganite No. 2 was prepared according to Gmelin (13). Twenty-one grams of cobalt sulfate and 12 g. of potassium permanganate were dissolved in 600 cc. of water. Six hundred cc. of 3 per cent hydrogen peroxide were then added. The precipitate was filtered, washed free of sulfates, dried, and heated. The copper-cobalt manganite was prepared according to the directions in the patent of the I. G. Farbenindustrie (18). To 500 cc. of a saturated solution of potassium permanganate was added 60 g. of cobalt sulfate and 50 g. of copper sulfate. Hydrogen peroxide was then added until the permanganate color was discharged. The precipitate was filtered, washed free of sulfates, dried, and heated. The copper manganite and cobalt manganite No. 1 were made similarly.

Aluminates

The aluminates may be prepared by heating the mixed oxides in the correct mole ratios. Hedvall (14) has prepared many of these and Holgersson (16) and Natta and Passerini (25) report spinel structures from x-ray studies. Most of the aluminates have very distinctive colors.

Copper aluminate No. 2 and nickel aluminate No. 2 were prepared from a solution of the nitrates in a 2:1 mole ratio of aluminum and the other metal by adding ammonium hydroxide to a slight excess and precipitating the hydroxides. The mixed hydroxides were filtered off, washed, dried, and heated. The other aluminates were prepared by evaporating the solution of the nitrates to dryness, decomposing the nitrates, and heating.

The results of the tests of the efficiency of the unsupported catalysts are summarized in table 1.

SUPPORTED CATALYSTS

Aluminum oxide was used as the support. A ready supply was found in Hydralo, a commercial granular and porous product containing some silica. Precipitated alumina was also used. Inasmuch as Hydralo takes up moisture from the air very readily, it was necessary to heat the catalysts and let them cool in a dry atmosphere just before testing. Moisture acted as a poison for these catalysts at moderate temperatures.

The supported cobalt catalysts were the same color as cobalt aluminate and apparently consisted of a surface layer of cobalt aluminate on the alumina.

Cobalt aluminate No. 3

To 10 g. of Hydralo was added 6 g. of cobalt nitrate dissolved in 40 cc. of water. The mixture was evaporated to dryness, the nitrates decomposed, and the material heated to 1000°C. for 1 hour.

TABLE 1

Efficiency of unsupported catalysts

CATALYST	HEATED 1 HOUR AT °C.	PER CENT OF CARBON MONOXIDE CONVERTED AT						
		50°C.	100°C.	150°C.	200°C.	250°C.	300°C	350°C.
Cobalt chromite No. 1	1000	0	0	0	55	100	—	—
Copper chromite No. 1	1000	0	8	60	100	—	—	—
Nickel chromite No. 1	1000	0	0	0	15	62	100	—
Nickel chromite No. 2	700	0	0	11	45	94	100	—
Zinc chromite No. 1	725	0	0	8	22	73	100	—
Zinc chromite No. 2	725	0	8	25	41	48	65	100
Mixed copper-cobalt chromite No. 1	325	40	100	—	—	—	—	—
Mixed copper-cobalt chromite No. 2	750	15	70	100	—	—	—	—
Copper cobaltite No. 1	950	0	10	78	100	—	—	—
Nickel cobaltite No. 1	950	0	30	80	100	—	—	—
Iron cobaltite No. 1	925	0	8	50	100	—	—	—
Iron cobaltite No. 2	925	0	15	55	100	—	—	—
Zinc cobaltite No. 1	925	0	20	62	100	—	—	—
Zinc cobaltite No. 2	925	0	10	60	100	—	—	—
Cobalt ferrite No. 1	975	0	0	18	66	100	—	—
Cobalt ferrite No. 2-A	700	0	2	16	50	90	100	—
Cobalt ferrite No. 2-B	975	0	0	21	60	90	100	—
Copper ferrite No. 1	975	0	0	7	41	87	100	—
Copper ferrite No. 2	700	0	4	25	68	87	100	—
Nickel ferrite No. 1	975	0	0	4	17	46	82	100
Manganese ferrite No. 1	975	0	0	0	6	15	38	58
Copper cobalt manganite No. 1	1000	0	0	3	12	23	42	59
Copper manganite No. 1	1000	0	0	78	100	—	—	—
Cobalt manganite No. 1	1000	0	0	18	45	77	94	100
Cobalt manganite No. 2	1000	0	0	2	7	30	57	78
Cobalt aluminate No. 1	975	45	70	100	—	—	—	—
Copper aluminate No. 1	975	0	0	25	100	—	—	—
Copper aluminate No. 2	975	0	8	75	100	—	—	—
Manganese aluminate No. 1	975	0	0	18	62	100	—	—
Nickel aluminate No. 1	975	0	0	9	58	90	100	—
Nickel aluminate No. 2	975	0	0	18	54	100	—	—
Zinc aluminate No. 1	975	0	0	0	0	0	0	28
Iron aluminate No. 1	975	0	0	6	25	70	100	—

Cobalt aluminate No. 4

A fresh layer of alumina was put on the surface of the Hydralo by adding 3 g. of aluminum nitrate in water to 10 g. of Hydralo, evaporating to dryness, and heating to 1000°C. This Hydralo was then treated as above.

Cobalt aluminate No. 5

Sixty-five grams of aluminum sulfate and 1.5 g. of cobalt nitrate were dissolved in 1000 cc. of water and ammonia added until just alkaline. The precipitate was washed, dried, heated to 1000°C. for 1 hour, washed until free from sulfate, heated to 1000°C. again, allowed to stand overnight in an ammoniacal solution of cobalt nitrate, washed until free from ammonia, and finally heated at 1000°C. for 1 hour.

Kleinstuck (19) reported that alumina took up metals from ammoniacal solutions of their salts and on ignition gave characteristic colors. He also mentioned that the blue-green copper compound oxidized warm methyl alcohol. Schenk (28) found that if not more than 5 per cent copper oxide was present in a precipitated mixture of copper and aluminum oxides the resultant mixture was grayish blue on ignition. The copper catalysts prepared were all bluish green in color. If too much copper were put in, they turned brown like copper aluminate. The catalyst was apparently a finely divided stabilized copper oxide.

Copper oxide No. 1

Ten grams of Hydralo was put in a solution of 2 g. of copper nitrate in 20 cc. of water. The mixture was evaporated, the nitrates decomposed, and heated to 925°C. for 1 hour.

Copper oxide No. 2

Two grams of aluminum nitrate in 20 cc. of water was added to 10 g. of Hydralo. The solution was evaporated to dryness, nitrates decomposed, and heated to 1000°C. for 1 hour. It was then put into a solution of 2 g. of copper nitrate in 20 cc. of water, evaporated to dryness, nitrates decomposed, and heated to 1000°C. for 1 hour.

Copper oxide No. 3

Ten grams of Hydralo was treated with a small amount of sodium silicate solution and heated to 1000°C. It was then put in a copper nitrate solution and the solution evaporated to dryness carefully so as not to decompose the nitrates. The residue was washed with water until the wash water showed no copper. The residue was dried and heated to 1000°C. for 1 hour.

Copper oxide No. 4

Ten grams of Hydralo was treated with ammonium hydroxide solution, the ammonia poured off, and immediately aluminum nitrate solution was added. This formed a gelatinous alumina around the Hydralo. This was washed, allowed to stand in copper nitrate solution, then washed until the wash water was free from copper, dried, and heated to 1000°C.

Copper oxide No. 5

Ten grams of Hydralo was allowed to stand in aluminum nitrate solution for several minutes and was then transferred into ammonium hydroxide solution. It was treated with an ammoniacal solution of copper nitrate, washed until free from alkali, dried, and heated to 1000°C.

Copper oxide No. 6

About 75 g. of anhydrous aluminum chloride was dissolved in 1500 cc. of water. The solution was heated to boiling and ammonia was added until the solution was decidedly alkaline. Then an ammoniacal solution

TABLE 2

Efficiency of supported catalysts

CATALYST	TEMPERATURE OF TEST	PER CENT CONVERSION
	degrees C.	
Cobalt aluminate No. 3	157	75
Cobalt aluminate No. 4	164	100
Cobalt aluminate No. 5	90	100
Copper oxide No. 1	161	50
Copper oxide No. 2	124	75
	154	100
Copper oxide No. 3	100	90
	118	100
Copper oxide No. 4	26	50
	70	100
Copper oxide No. 5	25	50
	55	75
Copper oxide No. 6	26	50
	70	100

of copper chloride was added until the supernatant liquid was dark blue. The precipitate was washed by decantation until free from alkali, filtered, washed, dried, and heated to 1000°C. for 1 hour.

OXIDATION WITH NITROUS OXIDE

In order to arrive at some mechanism for the catalytic action of the various catalysts, it was decided to use some other source of oxygen than that of the air. So a 40:60 mixture of nitrous oxide and nitrogen was used with 1 per cent carbon monoxide. The temperatures of 100 per cent oxidation in nitrous oxide and in air are given in table 3.

It will be noticed that the chromites, cobaltites, and manganites give 100 per cent oxidation at temperatures rather close together, while with

the aluminate and the copper oxide there is a wide discrepancy. In the first class are those compounds whose metal anion has a variable valence while in the other no such possibility exists. Lory (24) has shown that with air the chromites form a surface chromate which may be leached off with hot water. The amount of chromate may be determined by adding potassium iodide and titrating the liberated iodine with thiosulfate. Chromate formation was likewise proved here with the nitrous oxide. Five grams of copper chromite No. 1 was heated to 300°C. for 2 hours, leached with hot water, and chromate equivalent to 11.5 cc. of 0.01 *N* thiosulfate was obtained. It was heated again to 300°C. and then put in the nitrous oxide–nitrogen–carbon monoxide gas stream at 193°C. for 3 hours. At the end of that time a test showed 100 per cent oxidation of the carbon monoxide. The chromite was leached and showed a chromate equivalent of 5.8 cc. of thiosulfate. It was dried at 90°C. and then leached, showing a

TABLE 3

*Comparison of oxidation with nitrous oxide and air**

CATALYST	TEMPERATURE AT 100 PER CENT OXIDATION	
	Air	N_2O
Copper chromite No. 1	181	182
Cobalt chromite No. 1	252	250
Copper cobaltite No. 1	171	176
Copper manganite No. 1	198	185
Cobalt aluminate No. 1	156	170
†Copper oxide No. 6	25	250

* Mr. C. G. Albert made the tests with nitrous oxide.

† 50 per cent oxidation.

chromate equivalent of 0.8 cc. of thiosulfate. It was dried again at 90°C. and put in the train as before. After 4 hours in the gas stream at 196°C. the catalyst showed 100 per cent conversion. It was removed and leached and showed 2.2 cc. thiosulfate or nearly three times the amount of the blank (0.8 cc.). This indicates that the nitrous oxide oxidizes the chromite analogously to air, but not quite all the surface is oxidized,—only the more active spots and apparently these are the catalytically active spots. While the carbon monoxide is capable of reducing the whole surface, only the more active parts are oxidized by nitrous oxide and serve for catalysis. This serves to bear out further Lory's theory of alternate oxidation and reduction of the catalyst surface.

REACTIONS OF COPPER OXIDE NO. 6

Some copper oxide No. 6 was put in a tube between two gas burets and heated to 370°C. Nitrous oxide was passed back and forth over it without

any change in volume. Apparently it does not act as a catalyst for the dissociation of nitrous oxide. The fact that there is no free oxygen present in the nitrous oxide oxidation helps to account for the difference in temperature of equivalent conversions.

Hydrogen was passed over the catalyst at 175°C. Brownish copper-

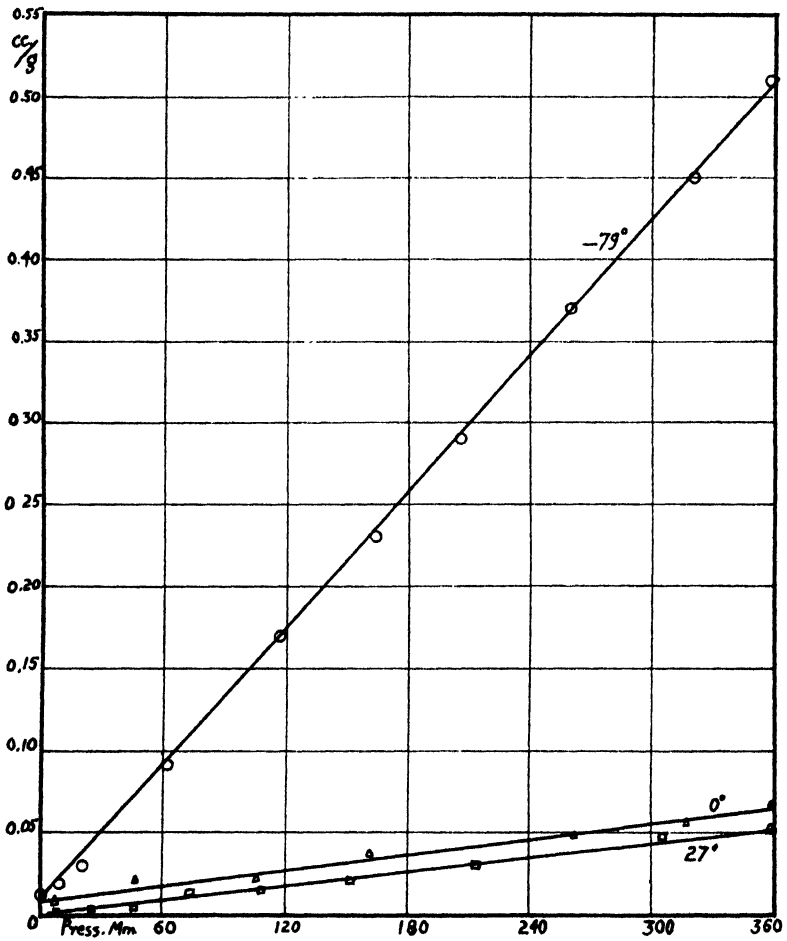

FIG. 1. ADSORPTION OF OXYGEN ON COPPER OXIDE NO. 6

colored spots appeared on the catalyst at different places and the spots gradually spread out until the whole catalyst was copper colored. On exposure to the air the catalyst slowly turned to its original bluish green with a distinct evolution of heat. The catalytic activity was the same at the end of the experiment. This indicated that the copper oxide was so finely divided that the reduced copper was almost pyrophoric.

Pure carbon monoxide was passed over the catalyst for 1.5 hours at 220°C., but no reduction was discernible, while hydrogen reduced the same catalyst completely in 10 minutes. Evidently an oxidation-reduction mechanism could not be used to explain the catalysis.

The adsorptive capacity of the catalyst for oxygen and for carbon monox-

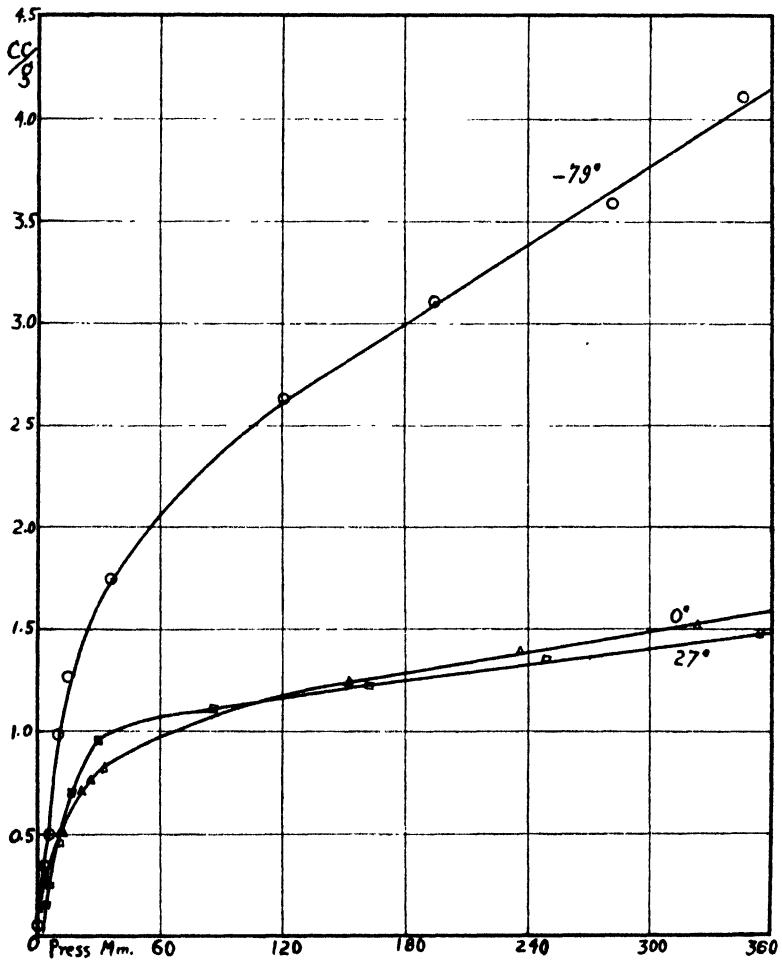

FIG. 2. ADSORPTION OF CARBON MONOXIDE ON COPPER OXIDE NO. 6

ide was then determined. The adsorptions were made in the customary way. A mercury vapor pump was used to evacuate the apparatus to 10^{-5} cm. or better. The catalyst was degassed at 375°C. overnight after each run. The gases were purified by standard methods. The dead space in the apparatus was determined with helium. The sample of supported copper oxide weighed 6.33 g. and the dead space was 10.9 cc.

The oxygen adsorption at all temperatures and pressures was instantaneous. The carbon monoxide adsorption was instantaneous at −79°C., but at 0°C. and room temperature there was an immediate adsorption followed by a slower adsorption which lasted from half an hour to four hours. The pressure decrease was rapid at first and then became progressively slower. This is indicative of chemical adsorption. The adsorption isotherms are shown in figures 1 and 2. The volume is calculated to standard conditions. They agree qualitatively with Benton's (4) adsorptions on copper oxide but show a larger adsorption, as would be expected from the more finely divided copper oxide. Adsorption measurements of oxygen, carbon monoxide, and carbon dioxide on copper chromite and other of the catalysts are now being made in this laboratory.

DISCUSSION OF RESULTS

From the standpoint of efficiency the supported copper oxide catalysts are by far the best of those reported, although several others give good conversion of carbon monoxide at moderate temperatures.

From the standpoint of the mechanism of the reaction it is possible to divide the catalysts into two groups,—those with a probable oxidation-reduction mechanism and those which probably do not have such a mechanism. The chromites, cobaltites, ferrites, and manganites may be put in the former class, while the aluminates and the supported copper oxides belong in the latter. It has been shown by Lory, and further substantiated by the present work, that there is a formation of surface chromate on the chromites and that this is reduced by carbon monoxide and oxidized by air and also nitrous oxide. These reactions indicate that the catalytic action is due to an alternate oxidation and reduction of the surface layer. The adsorption measurements being made here should throw further light on this.

On the other hand it appears that carbon monoxide will not reduce the copper oxide catalysts, and with the aluminates there is no possibility of valence change similar to that occurring with the chromites. The adsorption measurements show that carbon monoxide is chemically adsorbed on the surface of the copper oxide and also adsorbed very strongly, while the oxygen is adsorbed only slightly. Bone and Andrew (6) say that on ordinary copper oxide a layer of oxygen and nitrogen is adsorbed, that the oxygen is "activated," and that this oxygen oxidizes the carbon monoxide. However from the measurements made here it would seem that the carbon monoxide was the more strongly adsorbed and received an energy of activation due to adsorption and then reacted with the oxygen somewhat similarly to Langmuir's (21) explanation of the action of platinum on this same reaction.

SUMMARY

1. Methods of preparation and tests of eight chromite, six cobaltite, seven ferrite, four manganite, eleven aluminate, and six supported copper oxide catalysts have been given.

2. Further evidence has been advanced to show that the mechanism of the chromite catalysis is alternate oxidation and reduction.

3. The adsorption isotherms for oxygen and for carbon monoxide on a supported copper oxide catalyst at −79°C., 0°C., and 27°C. have been determined.

4. A mechanism for the catalytic action of the supported copper oxide catalysts has been proposed.

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SPECIFIC HEAT OF FURAN AND ETHYL ETHER VAPORS

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Inspection of the available data on the specific heats of gases and vapors reveals the fact that there has been very little experimental work published on the latter. This paper gives the results of investigations concerning the

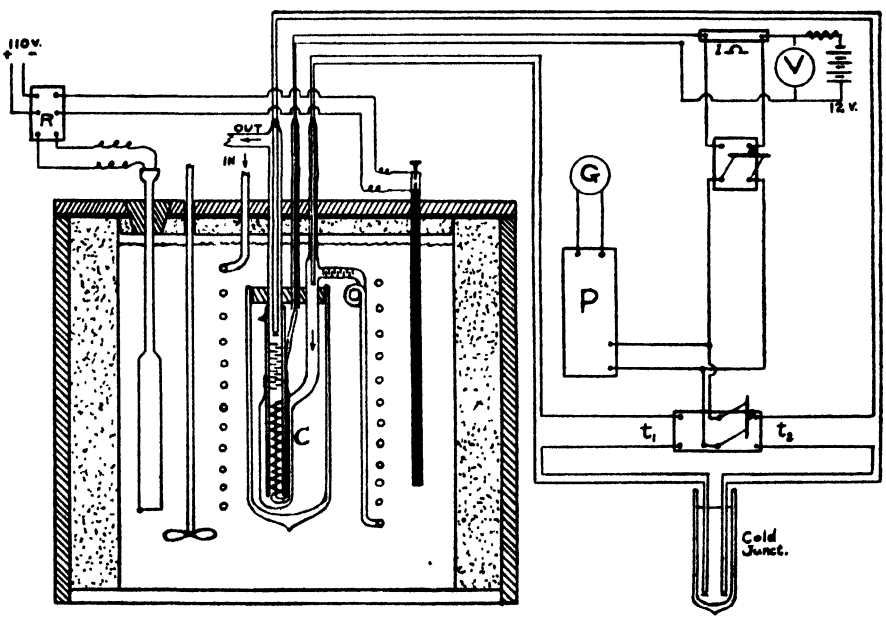

FIG. 1. FLOW CALORIMETER ASSEMBLY

effect of temperature on the specific heat at substantially one atmosphere for the vapors of the two compounds, furan and ethyl ether. The data were obtained by the constant flow method and cover a temperature range of approximately 45°C. to 100°C.

Figure 1 gives the essential details of the apparatus. The design was essentially that used by Buffington and Fleischer (1). The oil bath was controlled to ±0.1°C. by a Cenco relay. In the case of calibration the volume of gas was measured on the outlet side by means of a specially

designed Sprague gasometer which had been checked against a previously calibrated Sargent gas meter, the customary temperature and pressure corrections being made in every case. The ether and furan were vaporized from a brass boiler situated on a torsion balance, and recovered on the outlet side in a similar container immersed in an ice–salt mixture, with a vent to the atmosphere guarded by a calcium chloride tube. The boiler outlet tube was joined to the calorimeter inlet tube by means of a short rubber connection lined with tin foil. The boiler was wrapped with an insulated 110-volt heating coil, and various gas rates were obtained by adjustment of an external resistance in series with the heater. The inlet gas was brought to the temperature of the bath by passing through 8 meters of copper tubing immersed in the oil bath. The gas then passed over a 1-inch plug of copper gauze just before reaching the inlet thermocouple. The calorimeter proper was enclosed in a 500-cc. silvered Dewar flask immersed in the oil bath. The gas, after passing the inlet thermocouple, immediately entered the outer shell of the calorimeter proper, C, by way of two side-arm tubes. It then swept down the sides, over the heater leads, meeting the heating element at the bottom. The heating element consisted of a 75-ohm chromel "A" wire coil, supplied with current from lead storage cells, the amount of electrical energy being controlled by means of a slide wire resistance in series with the cells. The heater was enclosed in a double-walled, silvered Dewar tube, and provided with an insulated sheet metal radiation shield. After contact with the heater the gas passed over another plug of copper gauze just before reaching the outlet thermocouple. The thermocouples were made from No. 31 copper constantan wire and carefully calibrated over the range 0°C. to the boiling point of resublimed C.P. naphthalene. E.M.F. measurements were made with a Leeds and Northrup student's potentiometer, P, equipped with a Leeds and Northrup Type HS reflecting galvanometer, G. The voltage drop across the heater plus the standard 1-ohm resistance in series with it was measured by means of a voltmeter, V, checked against the potentiometer. The amount of current drawn by the heater was measured with the potentiometer from the drop in potential across the standard 1-ohm resistance. The electrical arrangement was designed to give continuous as well as accurate readings. The potentiometer was balanced against the standard cell before each run, and readings were taken over a period of twenty to thirty minutes after equilibrium had been reached. In the case of every gas, tests were made to ascertain the minimum gas rate above which the observed specific heat values were constant. For carbon dioxide this rate was found to be approximately 31 moles per hour, and for the other calibration gases approximately 35 moles per hour. For furan and ethyl ether the minimum gas rate proved to be 14 moles per hour.

A number of common gases including hydrogen, nitrogen, oxygen, carbon dioxide, and air were used for the purpose of calibration of the calorimeter. The hydrogen, nitrogen, and oxygen were of the laboratory grade as obtained from the Air Reduction Sales Co. The carbon dioxide was of a similar quality, obtained from Pure Carbonic, Incorp., Chicago,

TABLE 1

Flow calorimeter data and results for furan vapor at atmospheric pressure

RUN NO	HEAT INPUT	VAPOR FLOW	TEMPERATURE RISE	C_p (CORRECTED)
		At 44.33°C.		
	cal. per hour	*g per hour*	*degrees C.*	*cal. per mole per °C.*
1	533	1104	1 76	17 21
2	533	1146	1 69	17 29
3	533	1161	1.67	17.22
4	533	1020	1 91	17.17
5	533	1059	1 84	17.17
Average				17 21
		At 67.71°C.		
1	531	1275	1.40	18.67
2	390	1002	1.31	18.66
3	531	1092	1 64	18.61
4	531	1173	1.53	18.56
5	531	1146	1 57	18 53
Average				18.61
		At 98.99°C.		
1	529	1074	1.52	20 33
2	529	1110	1.48	20 21
3	530	1002	1.65	20 13
4	530	1143	1 44	20 21
5	530	984	1.65	20.49
6	527	1164	1 39	20 44
Average				20 30

Illinois. All were passed over phosphorus pentoxide before entering the calorimeter. The compressed air was tapped off the laboratory supply and passed over soda lime, anhydrous calcium chloride, and finally phosphorus pentoxide. The furan was prepared according to the method of Gilman and Lousinian (4) by the decarboxylation of furoic acid in the presence of a tar base and copper oxide as catalyst, and refractionated over

anhydrous calcium chloride. Results of the sodium fusion test for nitrogen in the final product were negative. The ethyl ether used was of the Mallinckrodt C.P. anhydrous quality. All specific heat measurements were made on a middle fraction of each liquid. After completion of all measure-

TABLE 2

Flow calorimeter data and results for ethyl ether vapor at atmospheric pressure

RUN NO	HEAT INPUT	VAPOR FLOW	TEMPERATURE RISE	C_p (CORRECTED)
		At 44.34°C.		
	cal. per hour	*g. per hour*	*degrees C.*	*cal. per mole per °C*
1	882	1206	1.74	28.75
2	878	1350	1.55	28 66
3	878	1412	1 48	28 68
4	878	1514	1.37	28 80
5	878	1226	1 70	28 75
6	697	1150	1 44	28 75
Average				28 73
		At 67.33°C.		
1	692	1329	1.17	30 45
2	872	1136	1 71	30 65
3	875	1384	1 42	30 37
4	1080	1420	1.69	30 64
5	875	1232	1.58	30 64
6	875	1288	1 51	30.74
Average				30.58
		At 99.16°C.		
1	872	1496	1.24	32 13
2	872	1342	1.39	31.94
3	870	1188	1 56	32.06
4	872	1118	1.65	32 31
5	872	1308	1 41	32.29
6	873	1190	1.56	32.12
Average				32 14

ments, the two liquids were redistilled. The boiling point ranges thus obtained were, for ethyl ether, 33.3°C. to 33.9°C., and for furan, 30.2°C. to 30.6°C., at 734.5 mm. The original calibration was then checked by a final run on hydrogen.

Tests made on the Joule-Thomson coefficient proved it to be negligible.

A total of twenty-two calibration runs was made and the values compared with those calculated from the equations presented by Eastman (3). In all cases the calibration factor proved to be essentially a constant, 0.923. The values as found in tables 1 and 2 are believed to be accurate within 1 per cent for the temperature range covered by the measurements, 45°C. to 100°C., and may be represented by the following equations of the type employed by Eastman (3) and many other investigators, t being °C.: for furan vapor, $Cp = 14.2341 + 7.188 \times 10^{-2} t - 1.071 \times 10^{-4} t^2$; for ethyl ether vapor, $Cp = 23.3833 + 14.71 \times 10^{-2} t - 5.929 \times 10^{-4} t^2$. The data presented on furan vapor are the first to be published, and those on ethyl ether are believed to be the best available for the temperature range covered by the measurements.

Values for ethyl ether vapor calculated from the equation here presented compare with those found in the literature as follows, at 80°C., in calories per mole per °C.: Dixon and Greenwood (2), 27.81; Wiedemann (5), 32.66; authors, 31.36.

SUMMARY

The specific heat of furan vapor at atmospheric pressure was measured in a flow calorimeter at 44.33, 67.71 and 98.99°C., the data fitting the equation:

$$CP \text{ (molal)} = 14.2341 + 7.188 \times 10^{-2} t - 1.071 \times 10^{-4} t^2 \ (t°\text{C.})$$

Similar data on ethyl ether were found to fit the equation:

$$CP \text{ (molal)} = 23.3833 + 14.71 \times 10^{-2} t - 5.929 \times 10^{-4} t^2 \ (t°\text{C.})$$

The authors wish to thank R. M. Buffington for suggesting the general problem of the specific heats of polyatomic vapors. Thanks are also due Henry Gilman for supplying the relatively large quantity of furan used.

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THE FREE ENERGY OF FORMATION OF LEAD AMALGAMS[1,2]

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INTRODUCTION

The thermodynamic properties of the alloys of mercury with various metals have been carefully studied, particularly in the cases of thallium and cadmium. While a number of measurements of the electromotive force of lead amalgam cells have been made, there has been no systematic study of these systems.

Puschin (7) measured the potential of lead amalgams against lead in normal lead nitrate over the range from 92.6 to 1.8 atomic per cent of lead. From pure lead to 66 atomic per cent the amalgams are single-phase and solid; from 66 atomic per cent to 1.8 per cent, the lowest concentration measured, the amalgams are two-phase. The solid phase is lead mercuride, Pb_2Hg, while the liquid phase is a saturated solution in equilibrium with the solid. Puschin found a potential of 0.0063 volt at 20°C. for all the two-phase amalgams. Below about 1.4 atomic per cent of lead, the amalgams are unsaturated.

Gerke (4), Carmody (3), and Spencer (9) have measured the potential of lead against the saturated amalgams. Spencer's value is given by the equation $E = 0.00552 + 0.0000137t$, which gives 0.00586 at 25.00°C.

Babinski (1) has measured the potential of lead against unsaturated amalgams at several concentrations. Richards and Garrod-Thomas (8) have measured the potentials of concentration cells, covering the range from 1.02 atomic per cent of lead to an infinitely dilute amalgam.

In this article are presented the results of measurements on the potential of lead against unsaturated lead amalgams and against two-phase amalgams of higher lead content than those previously studied, together with the activities and free energies of formation calculated from them.

[1] Contribution No. 275 from the Department of Chemistry, University of Pittsburgh.

[2] Submitted to the Graduate School of the University of Pittsburgh by Creig S. Hoyt in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

EXPERIMENTAL

For this purpose, cells were prepared as follows:

$$Pb \mid PbSO_4 \mid ZnSO_4 \mid PbSO_4 \mid PbHg_{sat'd.}$$

and

$$PbHg_{sat'd.} \mid PbSO_4 \mid ZnSO_4 \mid PbSO_4 \mid PbHg_{unsat'd.}$$

The chemical reaction occurring involves only the solution of lead in the amalgam in the first case and the transfer of lead from the more concentrated to the more dilute amalgam in the second. The zinc sulfate has no function save to decrease the internal resistance and thereby increase the sensitivity of the potential measurements.

PREPARATION OF MATERIALS

Lead

Lead for the amalgams and lead poles was Kahlbaum's "Lead for analysis" and gave the same potential as that prepared electrolytically. Lead electrodes were prepared by melting the freshly scraped bar, as furnished, under an atmosphere of hydrogen in a Pyrex tube and forcing the molten mass into a glass tube by the pressure of the hydrogen. The surface exposed to the electrolyte was scraped just before use. The platinum lead wire was cast in the electrode at the time of preparation.

Lead sulfate

Lead sulfate was prepared by precipitation from a solution of lead nitrate by zinc sulfate solution, according to the method of Bray (2), which is necessary to secure a reproducible potential at a lead–lead sulfate pole.

Mercury

Mercury was agitated with concentrated sulfuric acid and then distilled three times under diminished pressure according to the method of Hulett (5).

Lead amalgams

Lead amalgams were prepared by placing weighed amounts of mercury in a Pyrex separatory funnel with a capillary outlet. A rapid stream of hydrogen was introduced through an inlet tube sealed into the ground glass stopper, expelling the air from the flask through the outlet. Weighed amounts of lead sufficient to give lead amalgams of the desired concentrations were transferred to the funnels while the stream of hydrogen continued. The mixture was warmed and agitated until it was thoroughly homogeneous and then transferred to the cell while still at a temperature

high enough to insure that a one-phase amalgam remained. The capillary outlet served to remove any oxide coating which might collect on the surface.

Amalgams, which were only homogeneous at high temperatures, were prepared in a Pyrex test tube with a capillary outlet under an atmosphere of hydrogen and allowed to flow into the cell while still liquid.

Nitrogen

Tank nitrogen was freed from oxygen by the method of van Brunt (11).

Preparation of the cells

The cells used were of the H type and made of Pyrex glass. A platinum lead wire was sealed into the base of each shank and into a mercury well through which connection could be made to the potentiometer. Glass tubes were inserted through stoppers in each arm, connecting with a Pyrex flask containing the electrolyte. A stream of nitrogen was bubbled through the electrolyte and thence through the cell for four hours. When a neutral atmosphere in the cell was insured, sufficient amalgam was introduced into the arm to cover the platinum lead. The electrolyte was then forced over from the flask into the cell by the pressure of the nitrogen. The glass outlet tubes were sealed to make the cell gas-tight and it was transferred to the thermostat containing kerosene and regulated to 0.02°C. The cells came to equilibrium in about twenty minutes and gave stable potentials for several hours. After this, cells with lead poles gave a slow but steady drift. Cells having both amalgam poles gave stable potentials for a somewhat longer time, but in ten to fifteen hours a gradual change in potential began and no steady value was subsequently obtained.

The potentials were measured with a Leeds and Northrup Type K potentiometer, well shielded, using a No. 2500-c galvanometer. The standard cell was calibrated by the Bureau of Standards.

RESULTS AND COMPUTATIONS

Free energy of formation of the amalgams

Teeter (10) has discussed a method for calculating the partial molal free energies of amalgams and, hence, the free energy of formation per mole of amalgam.

For the reaction represented by the equation, N_2 moles Pb(solid) + N_1 moles Hg(liquid) = Pb(amalgam, N_2), Hg(amalgam, N_1) + ΔF the free energy change may be calculated by the equation,

$$\Delta F = N_1\Delta\overline{F}_1 + N_2\Delta\overline{F}_2$$

where $\Delta\overline{F}^1$ and $\Delta\overline{F}_2$ are the partial molal free energies of transfer of mercury and lead, respectively, from the metallic state to amalgams of concentration

N_1, N_2. The partial molal free energies must be multiplied by the respective mole fractions, since these indicate the number of moles transferred.

Now

$$\Delta\overline{F}_1 = -NFE_1 = RT \ln a_1$$

where a_1 is the activity of mercury in the amalgam, and

$$\Delta\overline{F}_2 = -NFE_2$$

E_1 and E_2 are the potentials of the cells in which the transfer of mercury and lead from the respective metals to the amalgam occurs.

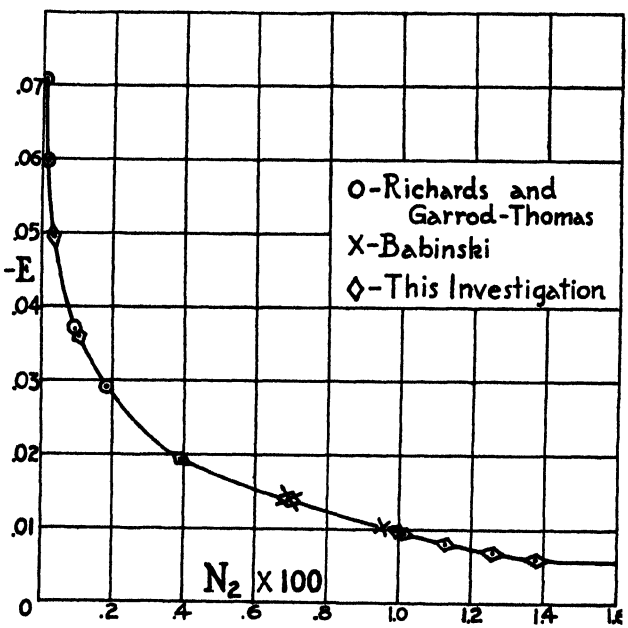

FIG. 1. E.M.F. OF LEAD AMALGAMS

The potentials of cells having the reaction

$$\text{Pb (solid)} = \text{Pb (amalgam, } N_2) + \Delta\overline{F}_2$$

for various values of N_2 have been determined by direct measurement and these have been plotted against the mole fraction of lead in figure 1.

By making a measurement of the electromotive force of one of the amalgams employed by Richards and Garrod-Thomas (8) against pure lead, the potentials of the amalgams employed in these concentration cells may be computed down to $N_2 = 0.000994$. By making the assumption that the activity coefficient of lead in the amalgams of Richards and Garrod-Thomas

at $N_2 = 0.000994$ and 0.000932 are identical, the potentials of the entire series out to a mole fraction of 0.000068 may be calculated. These values have been plotted on the same curve and show good agreement with the present series of measurements.

Two measurements of Babinski (1) are available and these are plotted with the other data.

By extrapolating the curve to $-E = 0.00586$, the upper limit of concentration of the one-phase amalgam is found to be $N_2 = 0.0143$. Above this concentration, the amalgam consists of the compound, Pb_2Hg, and a saturated solution in equilibrium with it.

TABLE 1

Free energy of formation of one mole of lead amalgam

N_2	$-E_2$	a_2/N_2	a_1/N_1	$-N_2\Delta\bar{F}_2$	$-N_1\Delta\bar{F}_1$	$-\Delta F$
	volts			*joules*	*joules*	*joules*
0 000068	0 07082	0 999	0 999	0 928	0 00	0 928
0 000160	0 05982	0 995	0 999	1 846	0 406	2 252
0 000354	0 04980	0 975	0 999	3 614	0 850	4 464
0 00102	0 03648	0 946	0 999	7 392	2 530	9 922
0 00180	0 02924	0 935	0 999	10 158	4 615	14 773
0 00405	0 01957	0 879	0 999	15 294	10 640	25 934
0 00697	0 01401	0 785	0 998	19 008	19 453	38 461
0 00994	0 00993	0 754	0 998	19 05	28 03	47 08
0.0113	0 00834	0 750	0 997	18 19	28 21	46 40
0 0126	0 00724	0 732	0 997	17 60	30 95	48 55
0 0138	0 00629	0 720	0 996	16 75	34 26	51 01
0 0200	0 00586	—	0 993	22 62	65 05	87 67
0 0400	0 00586	—	0 972	45 24	161 37	206 61
0 0600	0 00586	—	0 953	67 86	255 70	323 56
0 0943	0 00586	—	0 883	106 6	501 9	608 5
0 1728	0 00584	—	0.807	195 4	830 0	1025 4
0 286	0 00582	—	0 707	323 5	1209 5	1533 0
0 443	0 00567	—	0 546	501 0	1642 7	2143 7
0.475	0 00584	—	0 517	538 4	1699 8	2238 2

$\Delta\bar{F}_2$ is calculated directly from the measurements of the potential of lead against the amalgams and, when multiplied by N_2, gives the partial molal free energy of lead per mole of amalgam.

$\Delta\bar{F}_1$, on the other hand, must be calculated from the equation, $\Delta\bar{F}_1 = RT \ln a_1$, since the standard state is pure mercury.

Lewis and Randall (6) have shown that the activity of a metal in an amalgam may be computed from the potential of the amalgam against an infinitely dilute amalgam, by plotting $(-E/0.02982 - \log N_2)$ against N_2, where the metal is bivalent, and extrapolating the curve to $N_2 = 0$. Since the infinitely dilute solution is chosen as the standard state, we have a_2/N_2

= 1, when N_2 equals 0, or log a_2/N_2 equals 0. By subtracting this value of the ordinate from the ordinate at any other value of N_2, we obtain log a_2/N_2 at that point. Table 1 gives the activities of lead calculated in this manner, from the most dilute amalgam measured by Richards and Garrod-Thomas to a saturated amalgam.

Lewis and Randall (6) have shown that the activity of mercury in the amalgam may be calculated by plotting $(-E/0.02982 - \log N_2)$ against N_2/N_1 and solving for log a_1/N_1 by graphical integration. Table 1 shows the activities of mercury in the amalgams and the partial molal free energy of mercury per mole of amalgam.

TABLE 2

Heat of solution of lead in amalgams at 25.00°C.

N_2	E	dE/dT	HEAT OF TRANSFER	HEAT OF SOLUTION
	mv.	*mv.*	*joules*	*joules*
0.000068 0 000160	11 00	0 03696	3.86	11,007
0 000160 0 000994	23 28	0 0792	64 45	11,003
0 000994 0 00180	8 13	0 0282	53.65	10,938
0 00180 0 00405	9 67	0 0334	54 58	10,885
0 00405 0 0102	9 94	0 0391	331 55	10,830
0.0102 0 0142	4 02	0 2016	10,824 3	10,499
0 0142 1 0000	5 86	0 0140	−325 4	−325 4

The partial molal free energies of transfer of lead and mercury, respectively, from the pure metal to the amalgam are multiplied by the mole fractions of the respective metals in the amalgam. The sum of these quantities is equal to the free energy of formation of one mole of amalgam.

In all amalgams in which N_2 is greater than 0.0143, the same solid phase is present and the values of a_1/N_1 and a_2/N_2 in the liquid phase are constant, regardless of the mole fraction of lead in the whole amalgam. So long as only the liquid phase is considered, these values are 0.996 and 0.717, respectively. When one mole of amalgam, consisting of both liquid and solid phases, is the basis, the activities change with the mole fraction.

Heat of solution of lead in lead amalgams

Richards and Garrod-Thomas (8) have determined the temperature coefficients of lead amalgam concentration cells between 0.00°C. and 29.96°C. The heat of transfer may be calculated from this data using the equation of Gibbs-Helmholtz.

$$-\Delta H = 192{,}988\,[E - T(\mathrm{d}E/\mathrm{d}T)]$$

where $T = 298.16$. Table 2 shows the heat of transfer of lead in lead amalgams and the heat of solution from an infinitely dilute amalgam to saturation.

SUMMARY

Concentration cells having pure lead as one pole and lead amalgams of varying concentration as the other have been constructed and their potentials measured. Reproducible potentials are secured with amalgams up to 66 atomic per cent of lead. The amalgam is saturated at 0.0142 mole fraction at 25.00°C. and all amalgams between that concentration and 0.66 give the same potential.

The free energy of formation of amalgams up to a mole fraction of approximately 0.50 have been calculated as well as the activities of lead and mercury in the amalgams.

The heat of solution of lead in unsaturated amalgams has been calculated from the temperature coefficient of the electromotive force.

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THE LATENT HEAT OF FUSION AND IDEAL SOLUBILITY OF NAPHTHALENE[1]

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In some previous work from this laboratory (8) it has been shown that the solubility of naphthalene in chlorobenzene exceeds the ideal solubility as calculated from the generally accepted value of the latent heat of fusion of the naphthalene by means of the Schröder (6) equation. This result is not to be expected on account of the relatively non-polar character of both substances. Moreover, a determination of the heat of fusion by Bogojawlenski (2) gave a value considerably lower than that accepted, and one which would give an ideal solubility more nearly in accord with that obtained in chlorobenzene. With the above exception, the earlier determinations as summarized by Mathews (4) give a latent heat of fusion per mole of 4560 calories. This is the value accepted by the International Critical Tables. Later determinations by Andrews, Lynn, and Johnston (1) and Spaght, Thomas, and Parks (7) give 4540 and 4585 calories, respectively. The former value is probably more reliable, but the authors do not claim an accuracy of more than ± 1 per cent. In view of the uncertainty it was deemed best to make a more accurate determination of the latent heat of fusion of naphthalene and especially to measure the heat capacities of the solid and liquid in order to determine the variation of the heat of fusion with the temperature and thus to fix the exact form of the ideal solubility curve.

EXPERIMENTAL

Materials

Naphthalene ("Baker's Analyzed") was recrystallized three times from methanol and further purified by fractional freezing twice. Neither method alone gave a pure product, but the combination gave a material that on freezing shrank in volume by about 20 per cent and formed an almost perfectly transparent solid which clung closely to the walls of the tube leaving a clean core in the center. The same freezing phenomena had been previously observed in the case of very pure benzene prepared by the

[1] This work was made possible by assistance from a grant made by the Rockefeller Foundation to Washington University for research in science.

method of Richards and Shipley (5). The maximum amount of impurity which may be present in such materials is that which can form a saturated solid solution with the substance which freezes in the above manner, and perhaps a very slight amount which might be held in the interstices in the secondary or mosaic structure (10).

The melting point of the purified naphthalene was not less than 80.25°C. A sample from Kahlbaum and designated "for calorimetric purposes" showed the same melting point and was employed in a few determinations. The naphthalene was sealed up in soft glass tubes of about 9-mm. outside diameter and a wall thickness of about 0.5 mm. The total length of the tubes was about 18 cm. and the weight of naphthalene about 7 g.

The calorimeter

The container was a wide mouth Dewar flask of 1-liter capacity. This carried a closely fitting copper cover which extended on the outside about 3½ inches below the top of the calorimeter. The cover carried a small high speed turbine type of stirrer which revolved in a tube. There were also two holes with sliding covers for the admission of the sample and the thermometer, and a third very small hole for adjusting the level of the calorimetric liquid. The thermometer was of the platinum resistance type with a sensitive portion 10 cm. long and 1 cm. wide enclosed in a metal tube. It had been calibrated by the Bureau of Standards. A Mueller bridge was used to measure the resistance. Readings were made to 0.0001 ohm corresponding to about 0.001°C.

The calorimeter was clamped in the center of a 6-gallon earthenware jar filled with water until 2 inches of the calorimeter cover was immersed. The temperature of the water was regulated to ± 0.001°C. during the progress of the later calorimetric runs. To attain this constancy it was necessary to regulate the heating current and to stir violently with a large turbine type of stirrer. In some of the early determinations the regulation was to ± 0.01°C.

The calorimetric liquid was kerosene and the supply was kept constant by filling every day to a level exactly 3 cm. below the top of the cover. This adjustment was made by adding kerosene until the liquid rose in a small capillary tube at a calorimeter temperature of 22°C. The calorimeter was stirred at a constant rate of 1200 revolutions per minute by a small electric motor with a speed regulating device. The constancy of stirring during a run was tested by means of an A. C. neon light, applying the stroboscopic method to determine the rate of revolution of the pulley on the cover of the calorimeter. In a few of the earlier determinations the stirring rate was 1600 revolutions per minute and in others 1000 per minute.

The high temperature bath

This bath was made by winding a 1-inch round copper rod one foot long with nichrome ribbon, $\frac{1}{8}$ inch wide, No. 30 B & S, 0.43 ohm per foot. Thin asbestos sheet was placed between the ribbon and the rod, and the outside wound with several layers of sheet asbestos. The rod was bored from each end with a one-half inch hole and the upper end closed with a copper plug. Three and a half inches above the bottom of the furnace there was a small hole, through which a glass rod projected to hold the specimen in place. The temperature of the hot bath was determined by a single junction thermocouple constructed of No. 26 constantan and No. 28 copper wire. The hot junction was placed in a small hole bored parallel to the axis of the furnace and 4 inches deep. The electromotive force of the couple was measured by a Leeds and Northrup Type K potentiometer. The couple was calibrated in the same position in the furnace in which it was employed in the measurements. The standard instrument used for the comparison was a platinum resistance thermometer enclosed in glass, the sensitive portion being about 2 inches long. This portion was placed as nearly as possible in the position occupied by the specimen. Uniformity in this section was tested by raising and lowering the thermometer; the variation at 160°C. amounted to about 0.2°C. with a corresponding lower variation at the lower temperatures. It is estimated that the average temperature of the specimen under conditions of thermal equilibrium was known to less than 0.1°C., except possibly at temperatures above 130°C. In order to attain this accuracy it was necessary to heat with the current from storage batteries and to allow at least three hours from the start of the heating for the system to come to equilibrium. Even when changing the bath temperature but a few degrees, a 2-hour period was necessary for the temperature to become constant. It is probable that the greatest source of inaccuracy in the measurements was failure to attain equilibrium in the hot bath.

Calorimetric procedure

Before a run the temperature of the hot bath was read at intervals of five to ten minutes. When the temperature remained practically constant over such an interval, readings were made of the temperatures of the hot bath and the calorimeter on alternate minutes for a 10-minute rating period before the specimen was dropped into the calorimeter. After this, readings of the calorimetric temperatures were made during twenty minutes, for the first 2 minutes at half minute intervals and later every minute. The time intervals were observed on a stopclock which was started at the beginning of the run. The times between runs were in most cases sufficient to insure that the temperature of the calorimeter was not far from that of

the bath at the start of the procedure. It was seldom that more than three runs could be made in a single day.

The temperature rise Δt was calculated from the formula, $\Delta t = \Theta_3 - \Theta_2 + \eta$, where Θ_3 is the temperature at the end of the 10-minute calorimetric period and Θ_2 that at the beginning of this period. The extrapolation correction, η, was calculated by means of the modification of the Regnault-Pfaundler formula due to White (9).

The calorimeter equivalent

Three materials were used as a basis for the measurement of this quantity. The first was a sample of parting silver of 99.95 per cent purity cast in a graphite mold. The sample weighed 53.5 g. The second was a bar of annealed electrolytic copper weighing 84 g., and the third 5.55 g. of water sealed in the same glass as was used to contain the naphthalene specimen. The heat capacities for the copper and silver were obtained from the International Critical Tables. When the determinations were made the same day, the calorimetric equivalent showed the same value for the different samples. For example, the temperature rise was 2.471×10^{-3} °C. per calorie for the silver sample, while the corresponding figures for copper and water were 2.473 and 2.473. Other determinations showed essentially the same agreement. There was, however, a considerable change in the calorimeter equivalent with the time. The highest value over a period of four months was 2.498 and the lowest 2.452. The maximum deviation from the mean of 2.475 was 0.9 per cent and the average 0.3 per cent. Certain causes of such deviations are slight variations in the amount of calorimetric liquid and the mending of the basket for holding the calorimetric specimen, but the most important was a change caused by two periods of abnormally cold weather. The equivalent rose rather rapidly during these periods and subsequently declined over a period of about a week. This change was probably due to the loss of moisture from the calorimeter, due to extremely low relative humidity. No change in the calorimetric equivalent was found when the temperature of the hot bath was changed. The above changes in the calorimeter equivalent made necessary the determination of its value on practically every day upon which a run was made, especially in the case of the liquid naphthalene. The metal, usually copper, was heated to nearly the same temperature as that employed for the naphthalene or glass samples.

THE EXPERIMENTAL RESULTS

All the observations on naphthalene were reduced to a common calorimeter equivalent of 2.470×10^{-3} °C. per calorie and to a basic temperature of 22°C. Correction was then made for the glass which enclosed the specimen from a large scale curve drawn for that substance. The experimental

results were then plotted on a large scale, curves were drawn, and their equations calculated. The experimental results appear in tables 1 and 2.

TABLE 1

Molal heat content for solid naphthalene reckoned from a basic temperature of 22°C.

TEMPERATURE	H_s (OBSERVED)	Δ	TEMPERATURE	H_s (OBSERVED)	Δ
degrees C.	*calories per mole*		*degrees C.*	*calories per mole*	
36.67	588	0	74 21	2291	+24*
48 79	1096	+6	76 35	2375	+2
59.61	1563	−12	76 51	2412	+32†
65.48	1874	+26	76 69	2351	−38
66 41	1881	−10	77.08	2399	−10
68 33	1988	+13	77 37	2412	−11
69 28	2033	+4	79 59	2552	+18
72 58	2192	+4*	79 90	2750	+200

* Kahlbaum's naphthalene (for calorimetric purposes).
† Bath stirring irregular.

TABLE 2

Molal heat content of liquid naphthalene reckoned from a basic temperature of 22°C.

TEMPERATURE	H_l (OBSERVED)	Δ	TEMPERATURE	H_l (OBSERVED)	Δ
degrees C	*calories per mole*		*degrees C.*	*calories per mole*	
70 03	6550	+5	99.38	8062	+3
74.16	6755	+4	100.11	8030	−67‡
75 53	6825	+5	102.96	8230	−20
76.24	6863	+5	107 95	8480	−42
76 51	6863	−7	108 54	8540	−12
79 75	7050	+15	114 50	8865	−13
79 79	7025	−13	124 75	9460	+17
80 43	7058	−14*	128 46	9640	−12
81 09	7147	+42*	136 50	10150	+43*
81 77	7145	+6	137 86	10190	+2
84 00	7195	−59†	143 74	10510	−19
86 91	7370	+7	150 25	10920	+14
87.68	7460	+41	160 41	11515	+2
89.46	7520	−19	161 80	11560	−34
95.29	7840	−5	172.82	12210	−48

* Kahlbaum's naphthalene (for calorimetric purposes).
† Irregularity in calorimetric equivalent.
‡ Bath temperature not constant.

All observations made after a certain date are included except two or three for which a very definite reason for rejection could be assigned. The determinations on liquid naphthalene below 80°C. were made by first heating

the specimen above 90°C. for a considerable time and then cooling in the furnace until temperature equilibrium was reached. The sample of naphthalene from Kahlbaum did not supercool to any extent, but on fractional freezing behaved as regards supercooling in the same manner as did the highly purified material employed in most of the calorimetric determinations.

The values under the heading Δ in the tables indicate the deviations of the experimental results from the empirical curves employed to express the variation in the molal heat content with the temperature. The equations employed are $H_s = -781 + 33.17\,t + 0.1068t^2$ calories per mole for the solid, and $H_l = 3309 + 42.4t + 0.0546t^2$ calories per mole for the liquid, both values being calculated from a basic temperature of 22°C. The symbol t denotes the centigrade temperature.

The latent heat of fusion of naphthalene

When the equation for the heat content value for the solid is subtracted from that for the liquid, an expression is obtained for the value of the molal heat of fusion of naphthalene at various temperatures, at and below the melting point. The equation obtained is $\Delta H_f = 4090 + 9.23t - 0.0522t^2$. This indicates a value of the latent heat of fusion at 80°C. of 4495 calories per mole. The value at 70°C. is 4480 calories and at 50°C. this has fallen to 4420 calories. The results show a smaller variation of the latent heat of fusion with the temperature than is the case for most organic substances. In the list studied by Andrews, Lynn, and Johnston (1) only quinone and the aminobenzoic acids had smaller differences in the heat capacities of the solid and liquid substances at the melting point. In the latter substances the results were unsatisfactory owing to decomposition.

The ideal solubility of naphthalene

Lewis (3) defines an ideal solution as one that obeys Raoult's law at all temperatures and pressures, and shows that the formation of such a solution will take place from its component liquids without any heat of mixing or change in volume. This means for the ideal solution of a solid in a liquid that the heat of mixing shall be the heat of fusion of the solid at the temperature at which the solution is made. On this basis the ideal solubility may be calculated by means of a modification of the Schröder (6) equation which takes into account the variation in the latent heat of fusion with the temperature. The equation expressing this variation as given above is transformed into absolute temperatures giving $\Delta H_f = -2375 + 38.10T - 0.0528T^2$. This expression is not, of course, valid at temperatures much below 0°C. The above value is substituted in the equation

$$\frac{d \ln N}{dT} = \frac{\Delta H_f}{RT^2}$$

and integration gives

$$\ln N = 1195\left(\frac{1}{T} - \frac{1}{T_m}\right) - 19.17 \ln \frac{T_m}{T} + 0.02657(T_m - T)$$

where T_m is the absolute melting point of the naphthalene. In table 3 appear the values of the ideal solubility, expressed in mole fraction of naphthalene, as calculated by means of the above expression. The second column gives the results obtained when 353.4° was used as the absolute melting point of the naphthalene. This figure is probably within 0.05° of the melting point of perfectly pure naphthalene. Since in the investigation of the solubility of naphthalene (8) a material of an absolute melting point

TABLE 3

The ideal solubility of naphthalene

TEMPERATURE	MOLE FRACTION OF NAPHTHALENE Tm = 353 4	MOLE FRACTION OF NAPHTHALENE Tm = 353.15	MOLE FRACTION OF NAPHTHALENE SATURATED SOLUTION IN CHLOROBENZENE	MOLE FRACTION OF NAPHTHALENE ΔH_f CONSTANT AT 4495 CALORIES PER MOLE
degrees C				
70	0 819	0 828	0 830	0 829
62.6	0 714	0 716	0 716	0 717
60.0	0 678	0.681	0 682	0 680
50 0	0 551	0 553	0 555	0 551
49 0	0 540	0 541	0 540	0 540
42 8	0 471	0 473	0 473	0 470
40 0	0 442	0 444	0 444	0 441
30 0	0 351	0 352	0 352	0 348
29 4	0 346	0 347	0 349	0 342
22 1	0 290	0 291	0 292	0 285
20 0	0 275	0 277	0 277	0 269
10 0	0 213	0 214	0 215	0 205
8.8	0 207	0 207	0 208	0.198
4.2	0.183	0.183	0 185	0 174
0.0	0.163	0.163		

of 353.15° was employed, the ideal solubility was recalculated on that basis and the results appear in the third column. The experimental and interpolated values for the mole fraction of naphthalene when forming a saturated solution in chlorobenzene at various temperatures are shown in the fourth column. The values at the rounded temperatures are the interpolated values, while the others are the experimentally observed points from which the rounded values were obtained by graphic interpolation. These values are taken directly from the previous publication (8). In the last column of the table appear the values for the ideal solubility as calculated by the original form of the Schröder equation, using 4495 calories as the molal heat of fusion of naphthalene.

DISCUSSION

The value of the latent heat of fusion of naphthalene obtained in this investigation is about 1 per cent lower than the value found by Andrews, Lynn, and Johnston (1). A large part of the discrepancy can be accounted for by the fact that those investigators used the straight extrapolation method for obtaining the calorimetric temperature rise, while in this investigation a more exact modification of the Regnault-Pfaundler formula has been employed. In the determination of the calorimetric equivalent, under the conditions employed in this work, the two methods give almost identical results, but with the naphthalene the simple extrapolation gave considerably higher values for the reason that the heat was developed quite slowly at the beginning of the calorimetric period even though the time at which the fall of temperature became regular differed but little from the corresponding time for the copper sample. In one measurement for the liquid naphthalene at about 80°C. and the corresponding determination of the calorimeter equivalent, the extrapolation method gave a heat content per mole 45 calories higher than that obtained by the more exact method. For the solid naphthalene the heat exchange with the calorimeter was more rapid than for the copper sample at the same temperature. In this instance, therefore, the method of calculation would account for the difference between the results of Andrews, Lynn, and Johnston and those reported in this paper.

The measurement of the heat content of the supercooled liquid naphthalene is not important for the measurement of the variation of the latent heat of fusion with the temperature, since this variation is small and the degree of supercooling attained was not very great, but it does give a much greater certainty in obtaining the latent heat of fusion at the melting points, since the interpolation errors in the heat content curve for the liquid are considerably less than the extrapolation errors. The extrapolation errors in the heat content curve for the solid should be small numerically, since the extrapolation is carried over a short distance and the heat content is small. It is believed that a value for the latent heat of fusion of naphthalene of 4495 calories is accurate to within $\pm$ 15 calories.

It might be argued that a very long extrapolation of the heat content curve for the liquid is necessary to obtain the latent heat of fusion at the lower temperatures; this criticism is doubtless justified, but it is to be noted that the ideal solubility as calculated from an invariant heat of fusion does not differ appreciably from that taking into account such variation until a temperature at least thirty degrees below the melting point is reached. Even at the lower temperatures the discrepancies are not great and the correction introduced by employing the more exact formula is in the right direction and of the right order of magnitude to bring the ideal solubility

into close agreement with the observed solubility of naphthalene in chlorobenzene.

SUMMARY

1. Very pure naphthalene having a melting point of 80.25–80.3°C. has been prepared and some interesting phenomena on its freezing have been noted.

2. The latent heat of fusion of this material has been found to be 4495 calories per mole.

3. A reason has been suggested to account for the fact that this value is somewhat lower than the usually accepted value.

4. The ideal solubility of naphthalene has been calculated by a method which takes into account the variation in the latent heat of fusion with the temperature. The results show excellent agreement with previously published data on the solubility of naphthalene in chlorobenzene.

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THE DIFFUSION OF ELECTROLYTES IN SILICA GEL[1]

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INTRODUCTION

The purpose of this paper is to give quantitative methods for the preparation of impregnated gels of silica, and to explain the anomalous effect of high acid concentration on the washing of such gels. The first portion of the paper deals with the preparation of impregnated gels; the second with the measurements of the diffusion rates of acid and salts in silica gel. The results of the diffusion measurements give an explanation of the behavior of the impregnated gels during dialysis.

EXPERIMENTAL I

Analyses of material

In the preparation of silica gels, it is important to know the concentration of the sodium oxide and of the silicon dioxide, and the ratio of these two in the water glass in order to duplicate the preparations. This information is often absent from papers dealing with the formation of such gels. The analysis of the water glass used in our experiments is as follows: NaOH = 3.56 molar; SiO_2 = 6.67 molar; ratio SiO_2 to Na_2O = 3.75.

Preparation of the gels

The method used for the formation of the gels impregnated with heavy metal salts is similar to that of Klosky and Patrick (1). A measured volume of a salt of known concentration was added to a definite amount of 10 normal hydrochloric acid solution. Various volumes of standard sodium silicate solution were then added to this salt–acid mixture. The combinations employed are shown in table 1.

General method for preparation of impregnated gels of silica

As the presence of the salt has but little effect on the sol–gel transformation, a good gel containing any of the above salts may be obtained in the

[1] From the dissertation submitted by B. W. Allan to the Faculty of Philosophy of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1932.

following manner. To 30 cc. of 10 N hydrochloric acid and 10 cc. of any of the salts used above, add with constant stirring 100 cc. of 1 per cent sodium silicate solution. The rigidity of the gels may be increased by using a more concentrated solution of water glass. These gels should then be washed until acid-free.

Behavior of the gels on washing

After the impregnated gels were successfully prepared, it was decided to determine quantitatively the loss of heavy metal ion during dialysis. Two

TABLE 1

Preparation of gels impregnated with heavy metal salts

NO.	SALT SOLUTION		HYDROCHLORIC ACID 10 N	SODIUM SILICATE 1 PER CENT	REMARKS
	Concentration	Volume added			
			Iron gel		
		cc	cc	cc.	
1	0 1930 g.	5 0	2.5	100	Clear sol; no gel in two weeks
2	$FeCl_3$	5 0	3.0	100	Clear sol; no gel in two weeks
3	per cc.	5.0	6.0	100	Clear sol; gel in one week
4		5.0	4.5	25	Clear sol; perfect gel in two hours
			Copper gel		
1	0.2438 g.	5.0	5 0	100	Clear sol; no gel in one week
2	$CuCl_2$	5.0	3.0	100	Precipitate
3	per cc.	5.0	5.0	70	Clear sol; soft gel in one week
4		5.0	5.0	30	Clear sol; gel in two hours
			Manganese gel		
1	0.2148 g.	5 0	4.0	100	Clear sol; no gel in one week
2	$MnCl_2$	5.0	5 0	100	Clear sol; no gel in one week
3	per cc.	5.0	5.0	90	Clear sol; gel in one week
4		5.0	5.0	30	Clear sol; gel in three hours

gels impregnated with ferric chloride were prepared. One contained a small amount of acid, the other a large amount. Two gels containing copper chloride were prepared in a similar manner. These gels were carefully analyzed before and after sixty hours of dialysis. The results are given briefly in table 2.

Two important facts were obtained from these analyses. Salts which are easily hydrolyzed are retained more strongly than those which are not, and salts are held more tenaciously by gels which contain a large excess of acid.

EXPERIMENTAL II

It is obvious that experiments like those described above are laborious and time-consuming; therefore it was desirable to attack the problem in another manner. Plans were now undertaken to measure the rate of diffusion of salts and acid through pure silica gel. However, none of the orthodox methods for measuring diffusion rates is applicable to silicic acid gel, owing to its shrinkage during syneresis and to its lack of adhesion to glass.

Finally it was decided to prepare permanent discs of silicic acid, and to measure diffusion through them. A mold was made from which thirty-six discs, 2.60 cm. in diameter and 1.90 cm. in thickness, could be made at once. These discs were made by preparing a sol of silicic acid which was then poured into the mold and allowed to set until gelation had occurred.

TABLE 2

Behavior of the gels on washing

GEL	SAMPLE	EXCESS ACID PER 100 CC HYDROGEL	RATIO $\frac{\text{MOLES } SiO_2}{\text{MOLES Fe}}$	RATIO $\frac{\text{MOLES } SiO_2}{\text{MOLES Cu}}$
		moles		
Iron	Original gel	0.0173	6.94:1	
	Washed gel	0 0000	17.35:1	
	Original gel	0.4025	6.94:1	
	Washed gel	0.0000	16.69:1	
Copper	Original gel	0.0173		6.31:1
	Washed gel	0 0000		247 00:1
	Original gel	0.4025		6 31:1
	Washed gel	0 0000		151 62:1

They were then removed, dialyzed, and allowed to dry in the air several days. Of course the discs shrunk on drying. When they had decreased to a definite size, they were replaced in water. However after the gel discs had lost such a large amount of water, it was impossible to replace them in water without their cracking to pieces. This was due to surface strains brought about by the unequal absorption of water. By preparing a gel of low acid content this difficulty was overcome. The properties of this gel were superior to any of those previously prepared. The discs could be dried readily without breakage. A stream of water-laden air was passed over them in order to resaturate them gradually. After this treatment they could be replaced in water without any danger of breakage. On drying, all the discs did not shrink to the same size. Since only six discs were needed these could be selected with ease from the lot.

Figure 1 shows the apparatus in which the discs were employed. A series of such apparatus was arranged in a large air-bath thermostat which

was kept at a constant temperature of 32.50°C. A 20-liter aspirator bottle on the top of the thermostat acted as a distilled water reservoir. This was connected by glass tubing to a smaller aspirator bottle (2-liter) inside the thermostat. The small reservoir was so constructed that the water drawn from it was always under a constant pressure and temperature. A large tube (1.5 cm. in diameter) from which side arms protruded carried water from the small reservoir to each of the diffusion cells. These side tubes

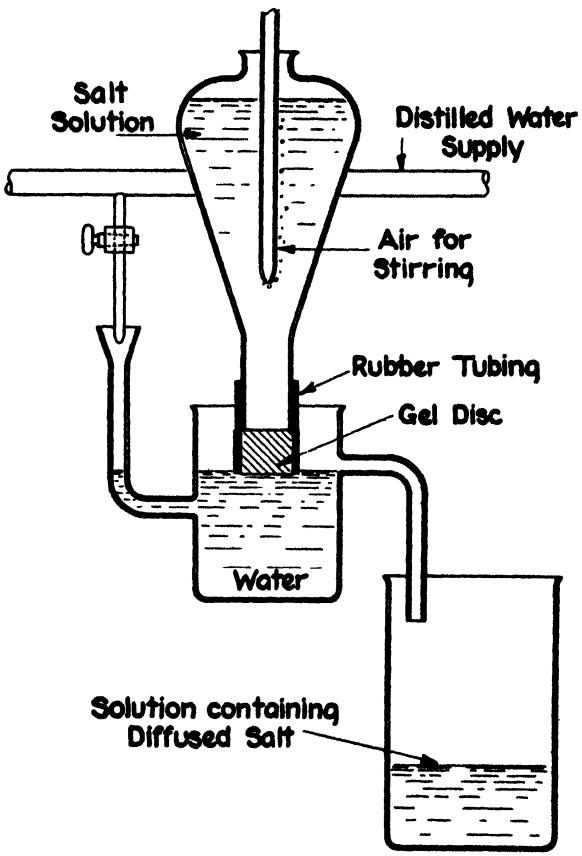

FIG. 1. APPARATUS USED IN MAKING THE MEASUREMENTS

entered the inlet tube of the cell. By means of stopcocks the flow of distilled water through these cells could be regulated. The rubber tubing in which the discs were held was attached to the reservoirs which were used to hold the salt solution. These salt reservoirs could easily be adjusted so that the face of the disc came in contact with the distilled water which flowed through the cell. After the salt reservoirs had been charged, the flow of water through the cells was regulated. The salt solutions were

stirred by bubbling air through them. This air had previously been saturated with moisture to prevent evaporation of the solvent from the salt solutions. Preliminary runs proved to be entirely satisfactory.

Measurements

The reservoirs were charged with their salt solution and the apparatus was adjusted and allowed to come to equilibrium. That is, diffusion was allowed to take place until the amount of solute passing through these discs per unit of time was constant. After this so-called "steady state"

TABLE 3

Results of the first run

NO.	SALT USED	ACID USED	CONCENTRATION OF SALT	CONCENTRATION OF ACID	TIME OF RUN	NaOH	$AgNO_3$	NaOH IN TERMS OF $AgNO_3$	GRAM-EQUIVALENT OF SALT DIFFUSED $\times 10^{-6}$
			N	*N*	*hours*	*cc.*			
1	LiCl	None	0 90	0	24	0	3 60		1.796
2	NaCl	None	0 90	0	24	0	6 40		3.193
3	KCl	None	0 90	0	24	0	8 95		4 470
4	LiCl	HCl	0 90	1 15	24	10 30	19 95	18 45	0 749
5	NaCl	HCl	0 90	1 15	24	12.80	25 50	22 95	1.273
6	KCl	HCl	0 90	1.15	24	13 30	27 55	23 80	1 872

TABLE 4

Average values of three runs

NO.	GRAM-EQUIVALENT OF SALT DIFFUSED $\times 10^{-6}$	DIFFUSION COEFFICIENT $\times 10^{-6}$
1	1.788	1 92
2	3 202	3.43
3	4.390	4.69
4	0.736	0.79
5	1.313	1.41
6	1.948	2.08

was reached, the liquid was removed from the cells, which were then thoroughly rinsed with distilled water. The flow of water through these cells was adjusted to the rate of 20 cc. per hour. Clean 800-cc. beakers were placed under each cell to catch the solution which flowed out of them. The thermostat was closed and the time recorded. After a definite time, approximately twenty-four hours, the run was discontinued. The solutions in the cells were removed and put in the beakers which had been placed under them. The cells were flushed out and this solution was added to that already in the beakers.

The salts used in these first measurements were lithium, sodium, and potassium chlorides; the acid was hydrochloric acid. The amount of diffusion was measured by analyzing the amount of salt and acid which came through the disc per unit of time. The amount of salt was determined by the method of Mohr, assuming that the concentration of the chloride ion gave a measure of the amount of salt present. Of course, in those experiments where both acid and salt were used, the concentration of the hydrochloric acid was first determined, then the total chloride con-

TABLE 5

The effect of different salts on the rate of diffusion of hydrochloric acid

NO.	SALT	CONCENTRATION	HCl (*M*)	NaOH (AVERAGE OF 3 RUNS)	DIFFUSION COEFFICENT (AVERAGE OF 3 RUNS)
		molar			
1	None	0	1 15	11 23	$8\ 61 \times 10^{-6}$
2	$CuCl_2$	0.3165	1 15	12 18	$9\ 33 \times 10^{-6}$
3	$FeCl_3$	0.2782	1.15	11 48	$8\ 81 \times 10^{-6}$
4	LiCl	0 9000	1.15	16.03	12.21×10^{-6}
5	NaCl	0.9000	1.15	16 80	12.78×10^{-6}
6	KCl	0.9000	1.15	16.15	$12\ 38 \times 10^{-6}$

TABLE 6

The effect of salts on the rate of diffusion of hydrochloric acid

NO	SALT	CONCENTRATION	HCl (*M*)	NaOH (AVERAGE OF 3 RUNS)	AVERAGE DIFFUSION COEFFICIENT
		molar			
1	None	0	1 150	11 01	8.43×10^{-6}
2	$CuCl_2$	0 6335	1.150	13 97	$10\ 71 \times 10^{-6}$
3	$FeCl_3$	0.5564	1.150	11.93	9.15×10^{-6}
4	LiCl	1.800	1.150	19 90	15.24×10^{-6}
5	NaCl	1.800	1.150	20.98	$16\ 29 \times 10^{-6}$
6	KCl	1.800	1.150	20.02	15.37×10^{-6}

centration. Obviously, the difference gave the amount of salt. Since the end points in these titrations are hard to observe, all the solutions were concentrated to a small volume and actual titrations were done in artificial illumination. Also a blank was run before each series of analyses. The results of the experiments are given in tables 3 and 4.

The discs employed had the following dimensions: diameter, 1.18 cm.; thickness, 0.91 cm.; area of face, 1.094 cm.^{2} The temperature of the thermostat was 32.50°C. Three such series of runs were made. The results in table 4 are average values of three runs.

It is seen from the results given in tables 3 and 4 that the order of the

diffusion coefficient is as follows: K > Na > Li. It is also shown that the diffusion coefficients of the salts are greatly affected by the presence of the acid. In each case the diffusion rate of each salt is diminished by the presence of acid.

Runs were now made to ascertain the effect of different salts on the rate of diffusion of hydrochloric acid. The discs employed had the following dimensions: diameter, 1.16 cm.; thickness, 0.90 cm.; area of face, 1.058 cm.^{2} The time of each run was 24 hours. The results are given in table 5.

The concentrations of the salts were increased. The time of each run was 24 hours. The results are shown in table 6.

Table 7 gives the results obtained on increasing the concentration of the ferric and cupric chlorides.

The results of these experiments are plainly visible. The diffusion rate of the hydrochloric acid was increased by the presence of salts.

TABLE 7

The effect of salts on the rate of diffusion of hydrochloric acid

NO.	SALT	CONCENTRATION	HCl (*N*)	NaOH (AVERAGE OF 3 RUNS)	AVERAGE DIFFUSION COEFFICIENT
		molar			
1	None	0	1 150	11 10	$8\ 52 \times 10^{-6}$
2	$CuCl_2$	1.00	1 150	16 98	$13\ 00 \times 10^{-6}$
3	$FeCl_3$	1.00	1.150	14.92	$11\ 43 \times 10^{-6}$

DISCUSSION

According to the Nernst theory of diffusion, which leads to the elementary explanation of the liquid potential, a mobile ion should increase the rate of diffusion of a more slowly moving oppositely charged ion. Furthermore, in the case of mixed electrolytes the more mobile ion will be retarded by the other ions, which in turn will experience an increase in mobility. This simple theory has been found to be in agreement with much experimental fact when dealing with ordinary diffusion phenomena. However, in the case of diffusion from a solution through a rigid gel structure, the above explanation no longer holds. Our washing of impregnated gels showed a marked retardation of the diffusion of the salt in the presence of acid, while our diffusion experiments through silica gel discs not only definitely proved the same point, but we were also able to show that the diffusion of the acid was speeded up in the presence of salt. These facts are in conflict with the Nernst theory; incidentally, Nernst never applied his ideas to systems such as used in this study.

One of the authors of this paper has recently developed a comprehensive theory which promises a satisfactory explanation of all the experi-

mental findings. Inasmuch as the development of the theory involves the discussion of much unpublished experimental work, it is thought inadvisable to attempt the argument at this time. Suffice it to say that it centers around an electrokinetic potential at the gel–solution interface.

SUMMARY

1. Quantitative methods have been worked out for the preparation of impregnated gels of silicic acid.

2. The anomalous effect of acid on the washing of such gels has been observed and an explanation has been advanced to account for the behavior.

3. Methods of preparing discs of silica gel, which permit the drying of such discs without shattering, have been discovered.

4. The diffusion of salts and acids has been studied in hydrated silica gel.

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SURFACE TENSION AND MOLECULAR VOLUME OF NITROGLYCERINE

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These measurements have been made in connection with the theory that the sensitivity of an explosive is associated with a state of "strain" within its molecule. An examination of the meagre results available hitherto gave some support to the theory, in that the value of the parachor appeared to be abnormal; no support, however, is given by the more carefully determined values that have now been obtained for the typical liquid explosive, nitroglycerine (glyceryl trinitrate).

PURITY OF SAMPLE

As received from the factory,[1] the nitroglycerine was absorbed in kieselguhr. It was recovered by displacement with water and was subsequently filtered through glass wool and muslin.

The composition was checked by measurement of the refractive index and the nitrogen content; the sample was thus shown to be free from detectable amounts of water and of glyceryl dinitrate.

The further examination was confined to the following overall test of the effect on surface tension of traces of impurities rather than to a detailed estimation of the amount of each impurity.

Effect of impurities

Impurities in a liquid are drawn into or away from the surface layer according as their presence lowers or raises the surface energy. In the former case, the lowering is disproportionately great, and a trace of impurity may produce an appreciable effect. A method of detecting this effect has therefore been devised on the following lines.

The effect is less pronounced with the freshly formed surface of a growing bubble than with a stationary surface confined in a capillary tube. In addition, therefore to measuring the surface tension by Sugden's (3) bubble-pressure method, measurements have been made by the capillary methods of Ferguson and Kennedy (1) and of Sutton (4). These capillary methods were designed for use when very little material is avail-

[1] Royal Gunpowder Factory, Waltham Abbey.

able, and are not as sensitive as the Sugden method; for the present purpose, however, they have the advantage that any error in the Sugden value due to impurity is magnified and detected.

Table 1 gives a series of values obtained with two samples of nitroglycerine insufficiently purified and a sample from the same source after further filtering and drying.

TABLE 1

Effect of impurities

SAMPLE	SURFACE TENSION MEASURED BY METHOD OF			REMARKS
	Sugden (3)	Ferguson and Kennedy (1)	Sutton (4)	
	dynes per cm.	*dynes per cm.*	*dynes per cm*	
I	49.8	45	42	After preliminary drying and filtering. Sample rejected
II	49.1	43	38	After preliminary drying and filtering. Sample rejected
III	50.3	50	51	Sample from same source as II. After further drying and filtering

TABLE 2

Parachor of nitroglycerine

TEMPERATURE	SURFACE TENSION	DENSITY	PARACHOR		METHOD OF MEASUREMENT
degrees C.	*dynes per cm.*				
20.5	50.4	1.595	379.3	mean 379.3	Sugden
20.5	50.1	1.595	378.7		Sugden
16.5	51.1	1.599	379.6		Sugden
16.7	50.8	1.599	379.1		Sugden
21.5	50.3	1.594	379.4		Sugden
21.5	50.3	1.594	379.4		Sugden
22.0	50.2	1.593	379		Ferguson
20.0	51.1	1.595	380		Sutton
20.1	50.4	1.595	379		Ferguson
17.2	51.4	1.599	380		Sutton
18.1	50.2	1.598	378		Ferguson
18.0	49.9	1.598	378		Ferguson

The effect of residual impurities is conspicuously greater when the Sutton or the Ferguson and Kennedy method is used. Agreement between the three methods is taken as an indication that the purity is adequate and the Sugden value is that given by pure nitroglycerine.

RESULTS

The measured values of the surface tension, the measured densities, and the values of the parachor derived from these are given in table 2. The agreement of the values obtained by the Sugden bubble-pressure method with those obtained by the capillary methods of Sutton and of Ferguson and Kennedy shows (see above) that the purity of the sample was adequate. The value found for the parachor, 379.3, may be compared with the value 378.9 which is obtained from the standard constants deduced by Sugden for carbon, hydrogen, oxygen, and the nitro group.

TABLE 3

"Parachor" of nitroglycerine–nitrobenzene solutions

I		II	III	IV	V	VI	VII
MOLAR COMPOSITION							
Nitrobenzene	Nitroglycerine	TEMPERATURE	SURFACE TENSION	DENSITY	"PARACHOR" OF SOLUTION (Calculated from Columns III and IV)	"PARACHOR" OF SOLUTION (Calculated from parachors of nitroglycerine and nitrobenzene)	DIFFERENCE
		degrees C	*dynes per cm*				
100 0	0 0					264 3	
84 5	15 5	20 0	43 6	1 269	281 8	282 2	−0 4
74 6	25 4	20 3	44 1	1 314	293 4	293 5	−0 1
65 9	34 1	19 9	45 4	1 351	304 9	303 5	+1 4
64 5	35 5	19 9	45 7	1 360	305 9	305 1	+0 8
		18 0	45 4	1 361	305 2	305 1	+0 1
		20 0	45 2	1 360	305 1	305 1	0 0
48 4	51 6	20 4	46 1	1 420	324 2	323 5	+0 7
24 2	75 8	21 5	46 8	1 507	350 4	351 4	−1 0
		20 0	46 9	1 507	350.5	351 4	−0 9
19 6	80 4	19 0	46 9	1 519	356 1	356 7	−0 6
13.6	86 4	18 0	48 7	1 550	363 1	363 5	−0.4
		20 0	48 7	1 549	363 3	363 5	−0 2
0.0	100 0					379 3	

Table 3 gives the measured surface tensions and measured densities of solutions of nitroglycerine and nitrobenzene. It also compares values of the "parachor of the solution" derived from these with those deduced from the measured values for nitroglycerine (379.3) and nitrobenzene (264.3) on the assumption that the parachor of a solution has the average value of the parachors of its constituents, calculated according to their molecular proportions (2). The parachor is shown to be an additive property of the constituents.

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THE REDUCTION POTENTIAL OF DEVELOPERS AND ITS SIGNIFICANCE FOR THE DEVELOPMENT OF THE LATENT IMAGE

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I. INTRODUCTION

The development of the latent image on a photographic plate is a chemical reaction, which may be represented by the following equation:

$$\text{Ag Br} + \text{Red.} = \text{Ag} + \text{Ox.}$$

We can imagine this reaction occurring in a galvanic cell at the electrodes of which the following two electron reactions take place:

$$\text{AgBr} + \ominus = \text{Ag} + \text{Br}^-$$

$$\text{Red.} = \text{Ox.} + \ominus$$

The electromotive force of this cell is:

$$E = \epsilon_{\text{Ag}} - \epsilon_{\text{Redox}} \tag{1}$$

The condition for reduction of the silver bromide is that the E.M.F. of this cell is positive. In this equation the silver potential is:

$$\epsilon_{\text{Ag}} = {}_{\text{Ag}}\epsilon_0 + \frac{RT}{F} \log L_{\text{AgBr}} - \frac{RT}{F} \log c_{\text{Br}^-} \tag{2}$$

in which L_{AgBr} is the solubility product of silver bromide. At 18°C. (2)

$${}_{\text{Ag}}\epsilon_0 = 0.808 \text{ volt}$$

and[1]

$$L_{\text{AgBr}} = 3.6 \times 10^{-13}$$

so that at 18°C.

$$\epsilon_{\text{Ag}} = 0.086 - 0.058 \log c_{\text{Br}^-} \tag{2a}$$

[1] According to our own measurements. R. Cavanagh (J. Chem. Soc. **1927**, 2207) found 3.13×10^{-13} at 16°C. Considering the large temperature coefficient this value agrees quite well with our measurements.

The concentration of the bromide in normal developers is about 0.01 molar.[2] Substituting this value in 2a, we obtain:

$$\epsilon_{Ag} = 0.202 \text{ volt at } 18°\text{C}.$$

The value of the redox potential will differ for the different developers. It is chiefly this value which determines the magnitude of E.

It may be expected that this last value will be of great importance for the rate of development. G. Bredig (1) was the first to draw attention to this point; he compiled a list of the reduction potentials of the various reducing agents which had been measured up to that time. His data relate however to rather arbitrary solutions and not to actual developer solutions. The great influence of the additions to these solutions, especially that of substances that alter the actual acidity, was not measured, so that no conclusions could be made about the relation between the reduction potential of a developer and its developing activity.

Other investigators as Sheppard and Mees (6), trying to measure the reduction potential of organic developers, found only inconstant and variable values. They consider, moreover, the reduction potential of little use in determining the reducing power, as other factors, such as the chemical resistance and the velocity of diffusion, interfere and will have a dominant influence on the velocity of reduction. Therefore these authors and also A. H. Nietz (4), instead of measuring the reduction potential along electrochemical lines, have sought a relation between the concentration of potassium bromide necessary to produce the same "density depression" at the same degree of development (γ) and the developing power of the developer. They introduce the term "relative reduction potential" and make the above-mentioned potassium bromide concentration proportional to this relative reduction potential. The real reduction potential cannot be calculated from their data, with the result that the relation between the real reduction potential and the developing power remains unknown.

II. THEORY OF THE LATENT IMAGE

Apart from the question about the importance of the reduction potential on the character of a developer, the knowledge of this potential is important for the theory of the latent image.

According to the germ theory of the latent image the first stage of the reduction process consists of a reaction of the reducing agent with the dissolved silver bromide, which results in the formation of a supersaturated solution of metallic silver. From this solution the silver may precipitate

[2] The German Committee for Sensitometry has, at the 8th International Congress for Photography in Dresden, 1931, proposed as normal developer a metol-hydrochinon developer with 1 g. of potassium bromide per liter, that is, 0.0085 molar Br^-.

if silver nuclei, formed by the action of light, are present. If however no nuclei are present, the reaction stops when a certain degree of supersaturation has been reached and an equilibrium has been established, which means that the reduction reaction is counterbalanced by the opposing reaction between the oxidation product of the reducing agent and the metallic silver atoms in the solution.

The concentration of the metallic silver in this solution is determined by the reduction potential of the reducing agent.

In order to compute this concentration, c, we will introduce c_0—the concentration of the metallic silver in a solution, which is in equilibrium with large silver particles or with a silver plate—in equation 2:

$$\epsilon_{Ag} = \epsilon_0 + \frac{RT}{F} \ln c_{Ag^+} = \epsilon_0' + \frac{RT}{F} \ln \frac{c_{Ag^+}}{c_0}$$

Now, if the concentration of the metallic silver is c instead of c_0, then

$$\epsilon'_{Ag} = \epsilon_0' + \frac{RT}{F} \ln \frac{c_{Ag^+}}{c} = \epsilon_{Ag} - \frac{RT}{F} \ln \frac{c}{c_0}$$

For equilibrium

$$\epsilon'_{Ag} = \epsilon_{Redox}$$

Thus:

$$\epsilon_{Ag} - \epsilon_{Redox} = \frac{RT}{F} \ln \frac{c}{c_0} \tag{3}$$

Introducing the value of ϵ_{Ag} at 18°C. in equation 2a, we obtain:

$$0.058 \log \frac{c}{c_0} = 0.086 - 0.058 \log c_{Br^-} - \epsilon_{Redox} \tag{3a}$$

In measuring the reduction potential we are now able to calculate $\frac{c}{c_0}$ and $\frac{c - c_0}{c_0}$, that is, the degree of supersaturation of the supersaturated silver solution.

M. Volmer (8), in a somewhat different way, viz., based on Sheppard's measurements of the equilibrium between silver, silver bromide and a solution of ferrous–ferric oxalate, made an estimation of the supersaturation in a normal ferrous oxalate developer, which is in contact with silver bromide. He arrived at the proportion $c:c_0 = 2000$, which he thought improbably high and he rejected the silver germ theory of the latent image on this ground. In a later publication (9) he thinks this proportion quite possible, however.

III. SOLUBILITY AND SIZE OF THE SILVER PARTICLES

In equation 3, c_0 represents the concentration of the metallic silver in equilibrium with large silver particles or with a silver plate. In the latent image, however, we are dealing with extremely small silver particles, which have a much greater solubility than compact silver.

The connection between the solubility and the dimensions of a particle is given by the equation of Thomson-Ostwald[3] (7):

$$RT \ln \frac{c}{c_0} = 2\sigma \frac{M}{d} \cdot \frac{1}{r} \tag{4}$$

in which c_0 is the solubility of large particles, c is the solubility of globular solid particles with the radius r, $\frac{M}{d}$ = molecular volume of the solid substance, and σ is the surface tension at the surface solid–solution.

For silver at 18°C. $\frac{M}{d} = \frac{108}{10.5} = 10.3$, $T = 291$, $R = 8.32 \times 10^7$. σ is unknown. We will take for σ the same value as for the surface tension of liquid silver against air at 950°C., namely 750 (3), although we have no reason to suppose that this is the right value. We find then:

$$\log \frac{c}{c_0} = \frac{2\sigma}{2.3RT} \cdot \frac{M}{d} \cdot \frac{1}{r} = 2.8 \times 10^{-7} \cdot \frac{1}{r} \tag{5}$$

It is clear that for all values of r greater than 10^{-5}, $\log \frac{c}{c_0}$ is very small and c practically equal to c_0.

For a particle of $10\mu\mu$ ($r = 5 \times 10^{-7}$ cm.) $\log \frac{c}{c_0} = 0.56$ and $\frac{c}{c_0} = 3.6$; for a particle of $2\mu\mu$, however, $\frac{c}{c_0} = 900$.

This shows that the value of c increases very rapidly, as the diameter of the particle decreases. A silver globule of $2\mu\mu$ diameter is still relatively large; it contains about five hundred atoms. The germs of the latent image are far smaller. According to the researches of Reinders and Hamburger (5), confirmed by quite other experiments of Chr. Winther (10), they will be aggregates of about four atoms. Equation 5 would give for such an aggregate a solubility nearly 10^{10} times greater than c_0.

Equation 4, however, is not applicable to such small particles, as the surface tension has lost its significance. The factor σ will just as well become a function of r and will diminish with r. Decreasing of r will therefore not increase the solubility as much as indicated by equation 4.

[3] Ostwald gave this formula with the coefficient 3 instead of 2. H. Freundlich (Kapillarchemie, 4th edition, Vol. I, p. 218) has demonstrated that this factor must be 2.

Qualitatively, however, we can say that with these small aggregates the solubility will decrease by steps as the aggregate increases with one or two atoms; the curve will have a shape as sketched in figure 1.

A solution of the concentration c will be just saturated with respect to particles of the size a. With respect to larger particles it will be supersaturated; hence these larger particles will act as germ and cause crystallization. With respect to smaller particles, the solution is unsaturated. These particles cannot act as germ; on the contrary they will dissolve.

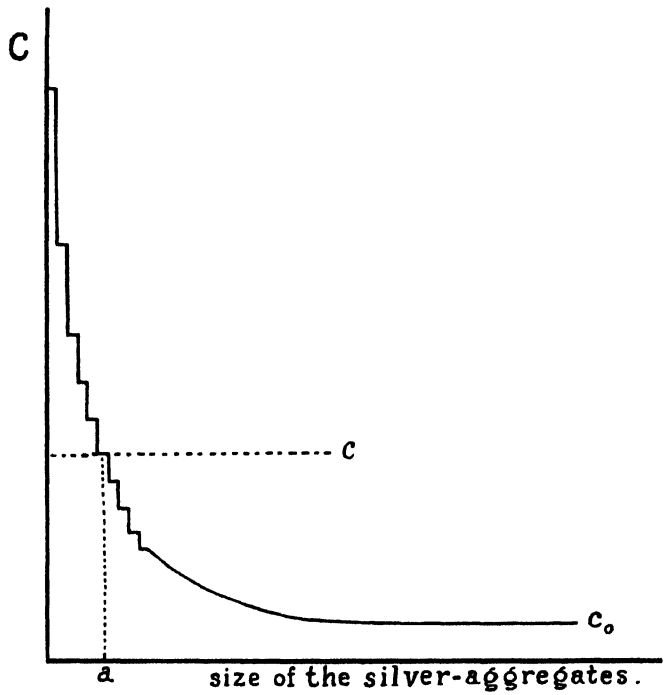

FIG. 1. SOLUBILITY OF SILVER PARTICLES AS A FUNCTION OF THEIR SIZE

Therefore, if in the latent image the germs have the size a, the developer must have a redox potential low enough to produce with the silver bromide a silver solution of a higher concentration than c, for it to be able to develop this latent image.

This redox potential must be lower than the redox potential that corresponds to the solubility of large silver particles.[4] By measuring the differ-

[4] We suppose the possibility of the spontaneous formation of nuclei in this case as excluded. For this spontaneous formation it would be necessary that the gap between single atoms and particles of the size a is bridged over, that the aggregation of these particles is established in some way or other. Without forming an exact idea about the mechanism of this process, it is obvious that in general it will be

ence $E = \epsilon_{Ag} - \epsilon_{Redox}$ that is just necessary to develop the latent image, we will be able to calculate the supersaturation, c, that corresponds to the solubility of the particles of the latent image.

IV. EXPERIMENTAL PROOF OF THE THEORY

To prove this theory experimentally one must have a set of solutions with ascending redox potential, each of which is quite constant and exactly measurable.

Such solutions can be made by adding various amounts of sodium citrate or sodium malonate to a mixed solution of a ferrous and a ferric salt. If the concentration of the iron salts is sufficiently high and the

TABLE 1

Measurement of redox potentials

Always 20 cc. of a solution with 0.125 mole $FeSO_4$ and 0.125 mole $Fe(SO_4)_{1.5}$ per liter

ABOVE SOLUTION + x CC OF 1 MOLAR SODIUM CITRATE		ABOVE SOLUTION + x CC. OF 1 MOLAR SODIUM MALONATE	
x	Redox potential	x	Redox potential
cc.		*cc.*	
0	+0 645	0	+0 645
1	0.625	1	0.620
2	0 600	2	0.596
3	0.545	3	0 552
3.5	0 480	4	0 477
4	0 380	5	0.380
4.5	0.265	6	0.262
5	0.205	7	0 175
6	0 150	8	0.122
7	0 110	9	0.092
8	0.085	10	0.071
9	0.070	12	0.050
10	0.060	16	0.021

proportion ferrous:ferric is nearly 1:1, then the solution has a great buffering capacity. The potential is very constant, and remains constant, also when the solution comes in contact with the air or after it has reduced a considerable part of the silver bromide in a plate to silver.

We made a solution of 0.125 mole $FeSO_4 \cdot (NH_4)_2SO_4 7aq$ and 0.125 mole $FeNH_4(SO_4)_2 \cdot 12aq$ per liter and added to 20 cc. of this solution increasing quantities of a 1 molar solution of sodium citrate or sodium malonate.

performed more easily, the narrower this gap is, that is, the smaller the particles a are. Spontaneous formation of nuclei, manifested by fogging of the plate, will thus appear more easily, the higher the supersaturation, that is, the lower the redox potential of the developer.

The redox potential of these solutions was measured with a platinum electrode at 20°C. and with a calomel electrode as second electrode. The values obtained are inserted in table 1 and in figure 2.

The potentials are very constant. Addition of 1 or 2 cc. of 0.1 normal sulfuric acid has little influence. The solutions are quite clear yellowish green and remain clear after standing for several days.

By increasing the proportion $Fe^{++}:Fe^{+++}$, the steep fall of the potential, which in the solutions of table 1 may be observed on addition of about 4 cc.

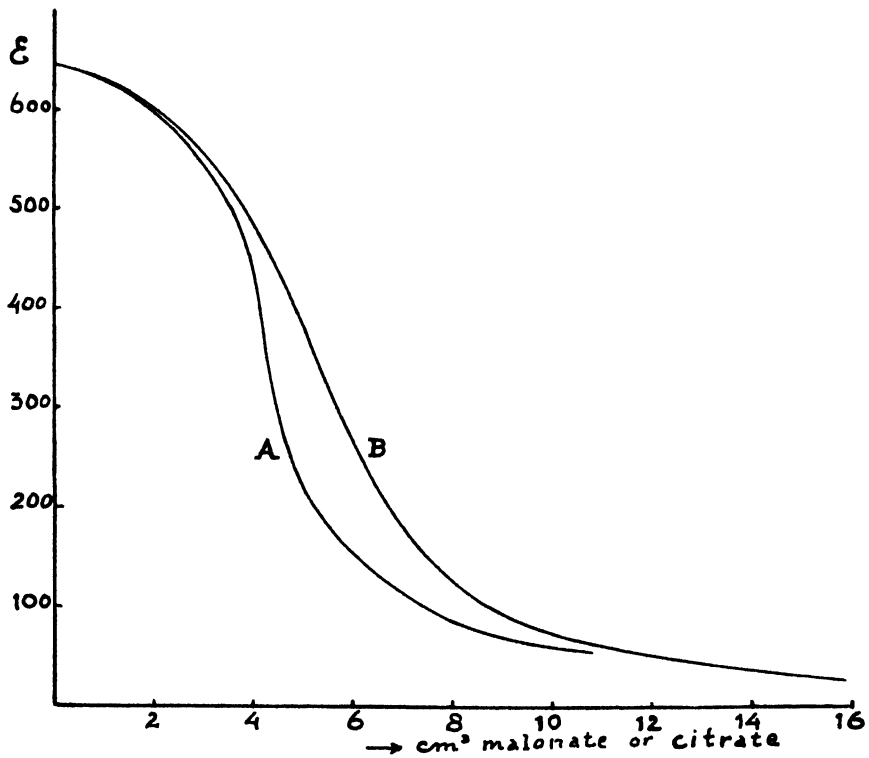

FIG. 2. REDOX POTENTIAL OF FERROUS-FERRIC SULFATE ON ADDITION OF SODIUM CITRATE OR SODIUM MALONATE

of citrate, sets in sooner, while also somewhat lower potentials may be obtained.

By selecting a proper proportion of the different ingredients, it is thus easily possible to prepare solutions in which the redox potential has any value desired between 300 and 0 millivolts.

V. VERIFICATION OF EQUATION 1

To verify now equation 1 and the conclusions that may be drawn from this equation, firstly it ought to be proved, that the reduction of silver

TABLE 2

Density of equally exposed strips of an Agfa Isochrom film, partly predeveloped to D=0.82 in metol-borax and then during twenty hours immersed in ferrous-ferric solutions with the indicated redox potential

NO OF STRIP	DENSITY OF THE PARTLY DEVELOPED HALF	DENSITY OF THE NOT PREDEVELOPED HALF	REDOX POTENTIAL	$E = \epsilon_{Ag} - \epsilon_{Redox}$
			mv.	*mv.*
1	0 16	0.10	303	−101
2	0 40	0 10	241	−39
3	0 82	0 10	202	0
4	0 82	0.10	200	+2
5	1 48	0 10	156	+46
6	2 53	0.15	113	+89
7	3 00	2 90	62	+140
8	3 00	3 00	22	+180
9	0 82	0 10		

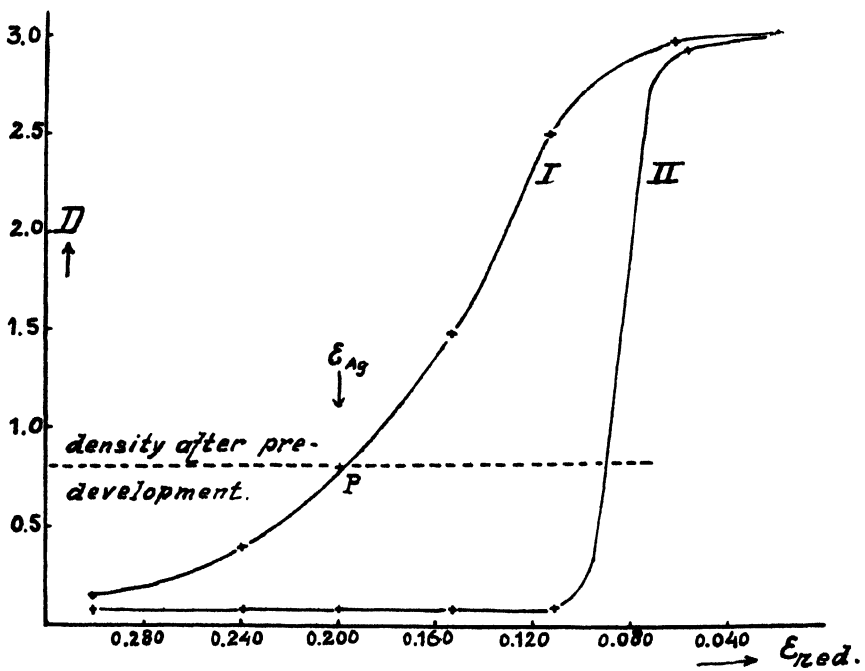

FIG. 3. DENSITY OF EQUALLY EXPOSED STRIPS OF AN AGFA ISOCHROM FILM AFTER IMMERSION IN FERROUS-FERRIC SOLUTIONS WITH THE INDICATED REDOX POTENTIAL

I, after exposure predeveloped in metol-borax; II, as I, but not predeveloped.

bromide proceeds in a developer solution with a lower redox potential than the silver potential and that resolution of reduced silver takes place in a solution with higher redox potential than the silver potential. For this purpose an Agfa Isochrom film was so long exposed, that, developed normally with a normal developer, it would obtain a density of about 3 (about 20 M.C.S.). The film was then half dipped in a metol-borax developer, wherein it obtained in 1 minute a density of 0.82.

The whole film was now thoroughly washed and cut in nine strips 1.3 × 9 cm., so that one half of each strip was partly developed to a density 0.82 and the other half was well exposed, but not developed. Eight of these strips were placed in tubes, nearly totally filled with 25 cc. of the above mentioned ferrous–ferric citrate solutions, which by addition of potassium bromide were made exactly 0.01 molar with respect to potassium bromide. The tubes were closed with a rubber stopper and during 20 hours kept at 18 to 20°C. The ninth strip, used for control, remained in pure water. After expiration of this time the strips were thoroughly washed and fixed, washed and dried. The density was then measured with the Goldberg densograph. The redox potential of the ferrous–ferric solutions was again measured as the strips were taken out. We found the results given in table 2.

In figure 3 the densities are represented in graph form as a function of the redox potential. The density 0.82, obtained by the predevelopment, is indicated by the dotted line, the final densities of the predeveloped parts by curve I, and those of the not predeveloped parts by curve II.

VI. CONCLUSIONS AS TO THE SOLUBILITY OF THE SILVER PARTICLES AND THE DEVELOPMENT OF THE LATENT IMAGE

From this experiment we may draw the following conclusions:

(1) The density arrived at by the predevelopment is intensified by a subsequent development in solutions with a lower redox potential than 200 millivolts and decreased by the subsequent action of a solution with a redox potential higher than 200 millivolts. The silver and silver bromide in the plates are thus in equilibrium with solutions containing 0.01 mole of potassium bromide per liter and having a redox potential = 200 millivolts. That, as we have seen on page 784, is exactly the potential of Ag/AgBr, 0.01 molar KBr in case of large silver particles. *This proves that the solubility of the silver particles in the developed plates is equal to the normal solubility of silver.*

Close to the equilibrium point P, curve I is nearly a straight line. Thus, the increase of density, which means the velocity of development, is proportional to the potential difference $E = \epsilon_{Ag} - \epsilon_{Redox}$, while also the decrease of density, that is the velocity of dissolution of silver, is proportional to the potential difference $\epsilon_{Redox} - \epsilon_{Ag}$.

(2) Curve II, giving the density by developing the latent image, is quite different. While the predeveloped part of the film is at once further developed as the redox potential sinks under the normal silver potential, the latent image shows no developing before the redox potential has reached the value 120 millivolts, that is, about 80 millivolts under the normal silver potential. As the difference $\epsilon_{Ag} - \epsilon_{Redox}$ increases, soon a normal developing is attained, giving the same density as the predeveloped films. Mr. M. C. F. Beukers has, on my request, repeated this experiment with other plates and other reducing solutions and obtained always similar results: *The development of the latent image does not begin before the redox potential of the developer has sunk 70 to 90 millivolts under the normal silver potential.*

VII. RESULTS OF SHEPPARD AND MEES

This result does not agree with the results of somewhat similar experiments described by Sheppard and Mees in their investigations on the theory of development. They determined the equilibrium

$$Ag^+ + Fe(C_2O_4)_2^{--} \rightleftarrows Ag(metal) + Fe(C_2O_4)_2^-$$

and found that the compositions of the mixtures of ferrous oxalate, ferric oxalate and potassium bromide, in which a negative of known density did not bleach further and of those in which the latent image of an exposed plate did not develop further, were practically equal. This would mean that curves I and II in figure 3 should coincide. Our experiments prove that this is not the case.

We cannot explain the discrepancy. Possibly Sheppard and Mees have used an extremely long exposure, so that the plate was partly blackened by the light. We must however remark that their experiments, in which they used 25 cc. of solution, containing at the utmost 0.000092 gram-mole of ferrous salt (equivalent to 0.5 cc. of oxygen), and mixed with a fifty times greater amount of ferric salt, cannot be very accurate. A slight oxidation of the ferrous salt will have a great influence on the redox potential.

VIII. SILVER PARTICLES IN THE LATENT IMAGE

From the conclusions mentioned in section VI it follows that the silver particles in the latent image have a much greater solubility than compact silver has. With the value $\epsilon_{Ag} - \epsilon_{Red.} = 0.080$, we can calculate the proportion $c:c_0$

$$0.058 \log \frac{c}{c_0} = 0.080 \qquad \text{or} \qquad c:c_0 = 25$$

The solubility of the silver nuclei in the latent image is, according to this formula, about twenty-five times as great as that of compact silver.

Equation 5 gives for the dimensions of these nuclei:

$$r = \frac{2.8 \times 10^{-7}}{\log c : c_0} = 2 \times 10^{-7} \text{ cm.}$$

Particles of this dimension will be aggregates of some hundreds of atoms. This is not in agreement with the results of Reinders and Hamburger which made it probable that these germs are aggregates of a very few atoms, e.g., 4 or 5. Now we have already demonstrated that equation 5 cannot be valid for such extremely small particles, as for those particles the value of σ will be only a fraction of the surface tension of compact silver. If we let σ equal not 750, but a value five times smaller, for instance, then we find $r = 3.6 \times 10^{-8}$ cm., a value that does agree very well with the results of Reinders and Hamburger.

TABLE 3

Redox potential of the solutions relating figures 4 and 5

NO. OF STRIP	REDOX POTENTIAL	$\epsilon_{Ag} - \epsilon_{Redox}$
	mv	*mv*
1	171	31
2	130	72
3	105	97
4	75	131

IX. DISAPPEARANCE OF THE LATENT IMAGE

Another conclusion may be drawn from the discussion in section III. The silver particles of the latent image, having a solubility that corresponds with a redox potential of 120 millivolts in a 0.01 molar potassium bromide solution saturated with silver bromide, are not in equilibrium with solutions with higher redox potential. In a solution with a redox potential between 200 and 120 millivolts—in which the partly developed silver bromide grains are further developed—these germs will dissolve. *The latent image will in these solutions diminish or disappear.*

This conclusion was proved in the following experiment: Five strips of the same film that had been used for the experiments in section V (Agfa Isochrom), numbered 1 to 5, were all exposed in the same way behind a Goldberg density wedge. Four of them were immersed in different ferrous–ferric citrate solutions, all containing 0.01 mole of potassium bromide per liter, and having a redox potential varying from 171 to 75 millivolts, as indicated in table 3. They remained in these solutions (in closed tubes) for 18 hours at 18°C. The fifth strip, used for control, remained during

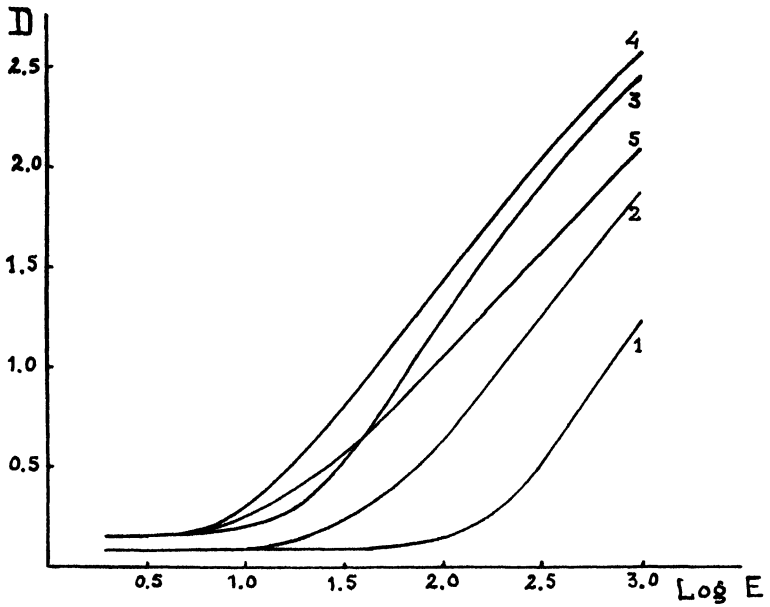

FIG. 4. CHARACTERISTIC CURVES OF AGFA ISOCHROM STRIPS, DEVELOPED IN A STANDARD METOL-BORAX DEVELOPER AFTER PRETREATMENT WITH FERROUS-FERRIC CITRATE SOLUTIONS OF VARIOUS REDOX POTENTIAL ϵ_{Redox} for 1 = 170, for 2 = 130, for 3 = 105 and for 4 = 75 mv. No. 5 untreated.

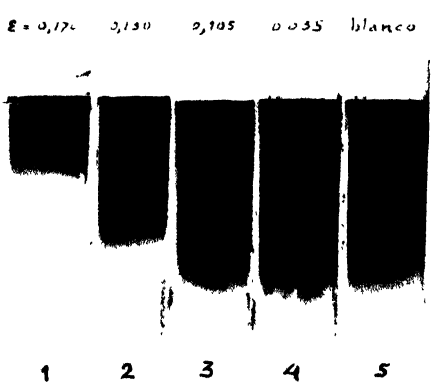

FIG. 5. STRIPS OF AN AGFA ISOCHROM PLATE, AFTER EXPOSURE BEHIND A DENSITY WEDGE, TREATED WITH FERROUS-FERRIC SOLUTIONS OF VARIOUS REDOX POTENTIAL AND THEN DEVELOPED IN A STANDARD METOL-BORAX DEVELOPER

this time in pure water. On expiration of this period, Nos. 3 and 4 were faintly developed in the more highly exposed parts; Nos. 1 and 2 were apparently unaltered. All the strips were washed for an hour in running

water and then developed for 6 minutes in a standard metol–borax developer,[5] fixed, washed and dried. Figure 4 gives the resulting characteristic curves. Figure 5 shows the developed strips of a duplicate experiment with Afga Isochrom plates.

The characteristic curves for solutions 1 and 2 lay beneath, those for solutions 3 and 4 somewhat above the control curve 5. In solutions 3 and 4 the redox potential is so low that $\epsilon_{Ag} - \epsilon_{Red.}$ surpasses the limit of 80 millivolts, mentioned in section VI. In these solutions the latent image is slightly developed and made visible by the subsequent development in the metol–borax solution.

In solutions 1 and 2, however, the latent image is partly dissolved, although the redox potential is below the normal silver potential in these solutions. This result is in perfect agreement with our predictions. It proves once more the far greater solubility of the silver germs of the latent image.

Comparing the form of the characteristic curve of the normally developed strip 5 with those of the strips that were pretreated with the iron citrate solutions, it is surprising to observe that the latter are steeper. Curve 3 and 5 even intersect, so that the weakly exposed parts in 3 are less developed than in 5, whereas the strongly exposed parts are more developed. This is what could be expected. Indeed, it is probable that the latent image in the weakly exposed parts will, on the average, be composed of smaller silver germs than those in the strongly exposed parts, so that they have a greater solubility. In a solution with a reduction potential about 90 millivolts lower than the normal silver potential in that solution, they will dissolve, whereas the larger silver aggregates will act as germ and will be developed.

This is an indication that the limit of 70 to 90 millivolts for the difference $\epsilon_{Ag} - \epsilon_{Red.}$, which must be surpassed to make the latent image developable, is not a constant value, but will depend on the exposure that has been given.

We will make further researches in regard to this point.

X. SUMMARY

1. The latent image of a normally exposed photographic plate is not developed unless the developer has a reduction potential of at least 70 millivolts below the silver potential in the solution.

2. From this fact it follows that the silver germs in the latent image have a solubility about twenty-five times the normal solubility of large silver particles.

[5] This solution contained in a liter: 0.05 mole metol (8.6 g.), 0.05 mole borax (19 g.), 0.05 mole sodium carbonate (5.3 g.), 0.3 mole $Na_2SO_3 \cdot 7H_2O$ (75 g.), and 0.5 g. potassium bromide. See Reinders, W., and Beukers, M. C. F.: Ber. 8th Intern. Kongr. Phot. Dresden, p. 171 (1931).

3. By addition of sodium citrate or sodium malonate to a mixture of ferrous and ferric salt, solutions with great buffer capacity may be prepared, having a reduction potential between 300 and 0 millivolts.

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THE COLOR AND CRYSTAL STRUCTURE OF PRECIPITATED CADMIUM SULFIDE

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Cadmium sulfide may be either yellow or red, depending on the conditions of formation. Earlier investigators (3) attributed this difference in color either to the presence of impurities or to the existence of yellow and red allotropic modifications of the compound. The possibility that the difference in color was due to allotropy was questioned by Allen and Crenshaw (1), who prepared crystals of the compound by a variety of methods and found them to be identical in structure with the mineral greenockite, irrespective of the method of formation and the color. It was concluded therefore that the differences in color were due to differences in the physical character, such as particle size and the nature of the surface of the particles, rather than to allotropy. The yellow form is usually obtained by precipitation from alkaline or cold solutions, and the orange or red from acid or hot solutions. Heating the yellow material gives an orange to red colored product, the change being more or less reversible on cooling (6).

In the absence of x-ray diffraction methods of examination, Allen and Crenshaw (1) were unable to determine the structure of the extremely minute crystals of the freshly precipitated salt and were forced to grow them to a size that could be observed optically, either by heating the dry powder or by digesting the mass under pressure at high temperatures. This always yielded hexagonal crystals like greenockite, but Böhm and Niclassen (2) showed by x-ray diffraction methods that the yellow precipitate thrown down from cadmium sulfate solution was cubic, being similar to the cubic zinc blende. This was confirmed by Ulrich and Zachariasen (5), who showed that cubic or β cadmium sulfide (a_0 = 5.820 Å.) was precipitated from a saturated cadmium sulfate solution by hydrogen sulfide and dried at 70°C. On heating this yellow cubic sulfide to 700–800°C. in the presence of sulfur vapor, hexagonal or α cadmium sulfide resulted. There is therefore no doubt of the existence of two polymorphic forms of the sulfide, but since both the cubic and the hexagonal forms may be yellow, it is obvious that the color differences are not due to polymorphism. Within the current year Müller and Löffler (4) precipitated cadmium sulfate solutions containing varying amounts of sulfuric acid with hydrogen

sulfide, and obtained precipitates which varied in color from yellow to red, the samples being more red the higher the concentration of acid. Since all of these preparations gave a cubic x-ray diffraction pattern, the differences in color were attributed to variation in particle size. It would appear

TABLE 1

Color and crystalline form of precipitated cadmium sulfide

CADMIUM SALT USED	WITHOUT THE ADDITION OF ACID				IN THE PRESENCE OF ADDED ACID			
	At 30°C		At 100°C		At 30°C.		At 100°C.	
0 1 *N*	Color	Crystalline form	Color	Crystalline form	Color	Crystalline form	Color	Crystalline form
Sulfate	Yellow	Hexagonal*	Yellow	Cubic	Yellow	Cubic†	Red	Cubic
Nitrate	Yellow	Hexagonal	Yellow	Hexagonal*	Yellow	Cubic†	Red	Cubic
Chloride	Yellow	Hexagonal*	Yellow	Hexagonal	Yellow	Hexagonal	Red	Hexagonal
Bromide	Yellow	Hexagonal*	Yellow	Hexagonal	Orange	Hexagonal	Red	Hexagonal
Iodide . . .	Orange	Hexagonal	Orange	Hexagonal	Orange	Hexagonal	Orange	Hexagonal

* Trace of cubic β cadmium sulfide

† Trace of hexagonal α cadmium sulfide

TABLE 2

X-ray diffraction data

α CADMIUM SULFIDE PRECIPITATED AT 100°C FROM $CdCl_2$, ACID		β CADMIUM SULFIDE PRECIPITATED AT 100°C FROM $CdSO_4$, ACID	
d_{hkl}	I	d_{hkl}	I
3 55	9	3.36	10
3.34	8	2.90	3
3.14	10	2 06	10
2.43	4	1 756	9
2 06	10	1 683	1
1.888	8	1 456	1
1.750	9	1 335	2
1.668	1	1 302	1
1.567	1	1 189	3
1 390	2	1.121	3
1 320	1	1.026	2
1.248	2	0 982	2
1.187	1		
1.150	1		
1.125	1		
1 066	1		
0.982	1		

from the x-ray studies of the gel that precipitated cadmium sulfide is always cubic, the hexagonal form resulting only after subjecting the gelatinous mass to high temperatures. Such is not the case, as the following experiments show.

EXPERIMENTAL

Hydrogen sulfide was passed into approximately 0.1 N solutions of cadmium sulfate, nitrate, chloride, bromide, and iodide at both 30°C. and 100°C. In a second series of experiments the solutions were made acid by the addition of 1 cc. of the corresponding "concentrated" acid to 50-cc. portions of the various cadmium salt solutions. The twenty samples were washed and dried at room temperature. Some of the samples from the bromide and iodide solutions formed very stable sols, and were precipitated by the addition of ether or alcohol. The various samples were examined by the x-ray diffraction method, using the General Electric diffraction apparatus. The observations of crystal form and color are listed in table 1. Typical patterns are shown in chart form in figure 1.

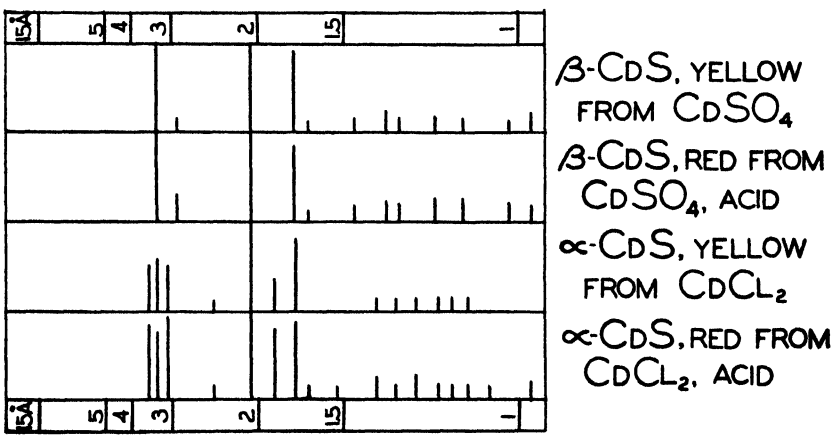

FIG. 1. α AND β CADMIUM SULFIDE PRECIPITATED AT 100°C.

Typical diffraction data are recorded in table 2; the values for the lattice constants of various samples agree within experimental error with the values of Ulrich and Zachariasen (5).

CONCLUSIONS

Inspection of the results in table 1 and figure 1 shows that either the cubic or hexagonal modifications of cadmium sulfide may be yellow or red (or orange), depending on the conditions of formation and treatment. All samples appear more or less orange upon grinding the dry aggregrates to a powder. The cubic form is usually obtained from the sulfate or nitrate solution, especially from hot or acid solutions. The hexagonal modification is usually obtained from the chloride, bromide, or iodide solutions. Small amounts of the cubic form sometimes occur in essentially hexagonal precipitates; this is probably more or less accidental, depending upon slight

variations in the conditions of precipitation. The difference in color must be attributed to difference in the physical character of the precipitate, such as particle size, the nature of the surface of the particles, and the state of aggregration. Difference in particle size alone will not suffice to explain all the known facts, since large crystals of greenockite are yellow, although red (or orange) particles are usually larger and more granular than the yellow ones. The view that color differences are essentially due to differences in physical character of the samples is in agreement with the observation that the red particles obtained from hot acid solutions possess less adsorptive capacity than the yellow particles formed in the cold (7).

SUMMARY

The following is a brief summary of the results of this investigation:

1. Either cubic β cadmium sulfide or hexagonal α cadmium sulfide may be yellow or red, depending upon the physical character of the precipitate.

2. The β cadmium sulfide tends to be precipitated from cadmium sulfate solutions, and under some conditions from the nitrate solutions, especially if the latter are hot and distinctly acid in reaction.

3. The α cadmium sulfide tends to be precipitated from the chloride, bromide, and iodide solutions, but these precipitates may also contain some of the β modification.

4. The lattice constants found for the two modifications of cadmium sulfide agree within experimental error with those of Ulrich and Zachariasen.

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LIQUID AMMONIA AS A SOLVENT. II

VAPOR PRESSURES OF SOLUTIONS AT 25°C.[1]

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These investigations were made in order to establish a significant scale of relative acidities, basicities, and salt-like properties in liquid ammonia and water. The present part deals with the vapor pressures of the more concentrated solutions of ammonium salts in liquid ammonia. These data may help to interpret the complex ammonia system of electrolytes.

EXPERIMENTAL

Manometer

The vapor pressures were measured directly on a manometer capable of reading fifteen atmospheres pressure (figure 1). The millimeter scale for this manometer was calibrated with a U. S. Bureau of Standards steel tape. The readings were corrected for temperature and gravity so that the vapor pressures are expressed in centimeters of mercury at 0°C. and a gravitational acceleration of 980.665 cm. per sec.[2] It was found that the correction for the compressibility of water only amounted to 0.001 per cent at 750 cm. pressure; it was therefore neglected. The manometer was filled with boiled water, all air bubbles being carefully removed. Columns A and F were carefully dried after the manometer was filled. The pressure of the water columns, calculated to standard conditions, was subtracted from the mercury reading and the barometric pressure added. As a final check on this method of measurement the vapor pressure of pure ammonia was measured. We obtained a value of 750.8 cm. as compared to 752.05 reported by Cragoe (1). When the initial pressure was not more than three atmospheres (concentrated solutions), a simple manometer was used.

Temperature

A double-walled copper container of 1-gallon capacity was immersed in a 75-gallon water thermostat. The Dewar containing the cell was placed

[1] This paper is a part of a thesis presented by W. E. Larsen in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Purdue University.

inside this adjustable container. This triplex system made it convenient to surround the cell with a carbon dioxide–ether bath for chilling and also to minimize temperature changes. The room was kept at a temperature

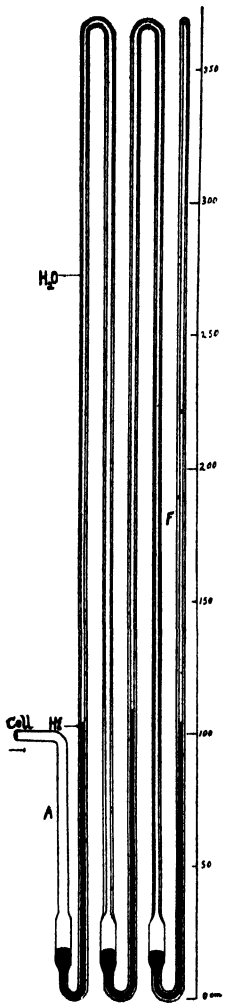


FIG. 1. MANOMETER

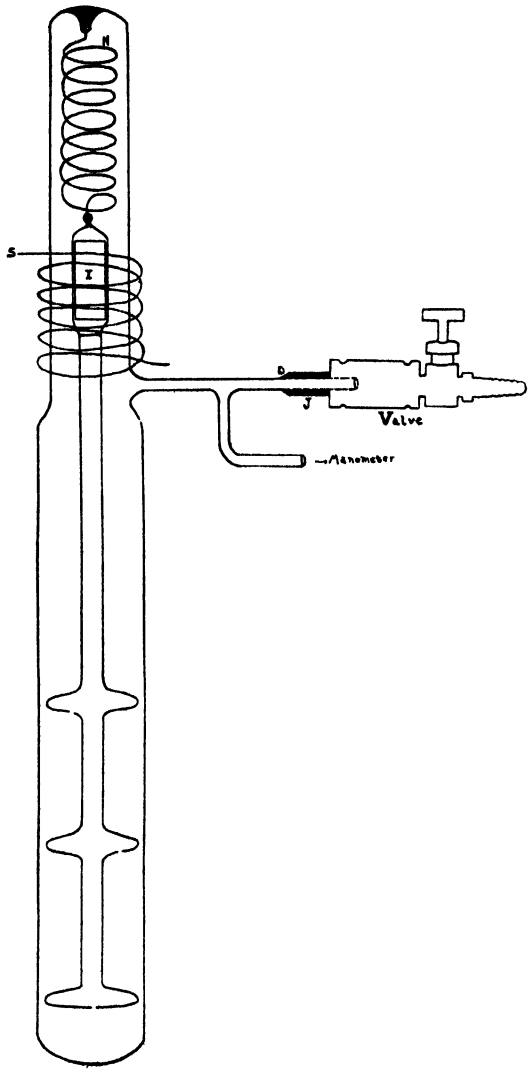


FIG. 2. THE CELL

such that the vapor pressure of ammonia was several centimeters above the vapor pressure of the solution, so that ammonia would not condense in the exposed tubes. The thermostat was kept at 25°C. ± 0.025°C., so the Beckmann (U. S. Bureau of Standards calibration) thermometer in the Dewar was constant to ±0.001°C. over a long period of time.

Cell

Figure 2 shows the electrically stirred cell used for the solutions. An intermittent current passed through S. V is an iron needle valve used in valving the ammonia when it was desired to change the concentration. The cell had a volume of 100 ml. The vapor space over the solution and in the tube leading to the manometer was measured gravimetrically. This space is reduced to a minimum.

Measurements

Reagent grade salts were recrystallized from water three times and dried for several hours at 110°C. They were placed in the cell and an

TABLE 1

Vapor pressures of ammonium nitrate in liquid ammonia at 25°C.

SERIES	MOLES NH_3 / MOLE NH_4NO_3	P	SERIES	MOLES NH_3 / MOLE NH_4NO_3	P
		cm. Hg			*cm.* Hg
A	0 744	86 3	C	8 01	613 0
B	0 808	86 3	D	9.10	638.1
A	1 22	88 0	E	11 4	672 6
C	1 30	97 0	F	12 2	682 7
C	1 56	123 0	E	15 6	699 2
B	1 76	143 4	E	21 7	716 6
A	1 85	152 9	F	32 6	727 9
D	1 93	163 5	E	47 3	735 5
D	2 20	192 6	E	51 8	736 6
C	2 58	235 8	G	60 0	738 7
D	2 84	266 7	G	69 7	740 4
C	3 09	291 4	G	80 6	741 7
C	3 45	331 1	G	91 4	742 6
C	4.01	385 9	G	111	743 7
D	4 55	438 6	F	126	744 4
D	5 23	489.1	F	135	744 8
D	6 30	551 1	F	140	745 0
C	7 05	580 7			

excess of ammonia condensed into it. The cell was then sealed in place and the system evacuated while chilled. The cell was then warmed with the valve closed until the vapor pressure was several atmospheres. By repeated warming, chilling, and pumping out, the cell and manometer were freed from air. In order to keep the ratio of ammonia in the solution to ammonia in the vapor phase high, it was necessary to use larger amounts of ammonia for the dilute solutions. The series varied from 13 g. of salt and 3 g. of ammonia to 0.4 g. of salt and 20 g. of ammonia. From three to

six hours were allowed for equilibrium to be established for the first reading and at least two hours for each subsequent reading. The manometer readings did not vary more than 1 mm. on standing an hour after equilibrium was reached.

The concentration was changed by allowing ammonia to escape through V and absorbing it in concentrated sulfuric acid. The concentration of the

TABLE 2

Vapor pressures of ammonium iodide in liquid ammonia at 25°C.

SERIES	$\frac{\text{MOLES } NH_3}{\text{MOLE } NH_4I}$	P	SERIES	$\frac{\text{MOLES } NH_3}{\text{MOLE } NH_4I}$	P
		cm. Hg			*cm* Hg
B	1 98	73.6	D	9 64	612 4
A	1 99	73.8	E	10 2	621 8
C	2 40	84.2	E	11.1	638 3
B	2 59	96.0	F	12 3	654 7
B	3 00	132 8	G	15 5	683.3
A	3 26	158 7	G	16 9	691.1
A	3 57	195 7	G	18 4	697 5
C	3.68	210 3	F	20 1	704 1
A	3.79	221.0	F	21.2	708 0
E	3 84	232.4	G	23.8	712 4
C	3 94	241.1	H	30 2	722 0
E	4 03	255.4	H	36 7	727 8
E	4 25	282 3	H	44.6	732 1
D	4 35	301.3	H	48 0	733 4
E	4.55	316.7	H	60 0	737.2
D	4 87	358 2	I	66 5	738.8
F	5 03	375 5	I	83 1	740.9
D	5 37	406 0	I	99 9	742 6
D	5.88	448 6	J	115	743 6
D	6 29	477 3	J	135	744 9
E	6 51	487 5	J	147	745 1
F	6 97	517 4	J	161	745 7
F	7 74	553 0	J	177	746 0
D	8 48	580 7	J	200	747 1

solution was calculated from the solvent and solute present in the cell at each reading, allowance being made for the ammonia in the vapor phase.

The weight of salt was determined at the end of a run by weighing the cell and salt and then weighing the cell after the salt had been dissolved out.

RESULTS AND CALCULATIONS

The values given in tables 1, 2, 3, and 4 are the values obtained from several sets of independent measurements. These values of the vapor pressures are plotted in figures 3 and 4, where the concentration is ex-

TABLE 3

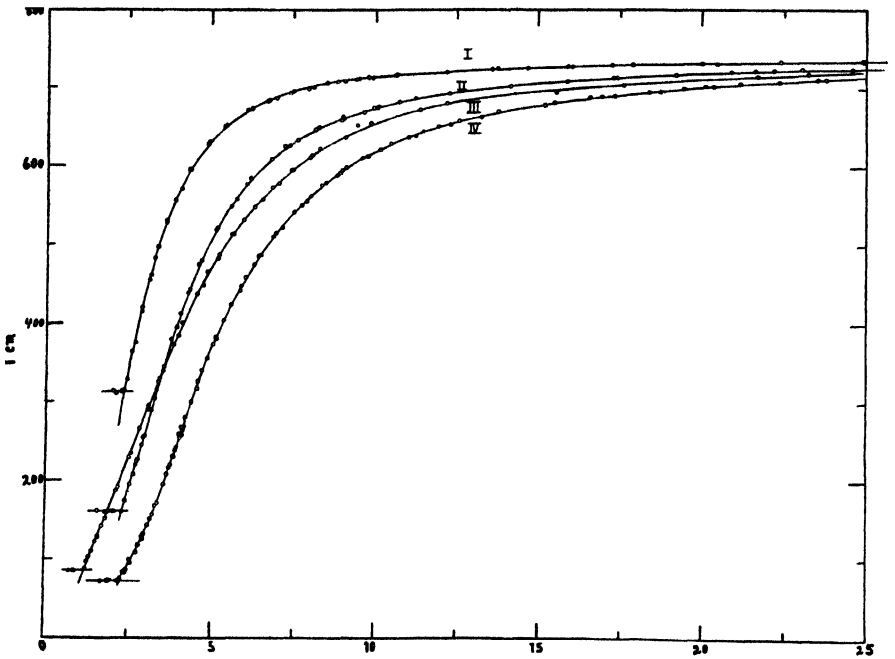
Vapor pressures of ammonium bromide in liquid ammonia at 25°C.

SERIES	MOLES NH_3 / MOLE NH_4Br	P	SERIES	MOLES NH_3 / MOLE NH_4Br	P
		cm. Hg			*cm* Hg
A	1 56	162 3	C	9.65	671.1
A	1 83	162 3	D	10.7	683 4
B	2 29	162 3	E	12 3	695 1
B	2 50	184 2	E	14 2	704 3
C	2 56	196 5	F	17.5	713.5
C	2 77	226 0	F	21 6	722 2
B	3 00	257 9	F	24 6	725.4
D	3 29	305 5	F	35 1	732 5
C	3 53	340 6	G	39 9	734 9
C	3 93	396 2	F	44 0	735 9
C	4 30	440 1	G	56 3	739.2
C	4 69	480 8	G	71 6	741.5
D	5 17	522 6	H	94 0	743 2
D	5 57	550 7	H	129	745 1
C	5 74	559 7	H	146	745 5
D	6 80	609 0	H	159	745.9
D	7 39	628 1	H	172	746 3
C	9 03	662 5			

TABLE 4

Vapor pressures of ammonium chloride in liquid ammonia at 25°C.

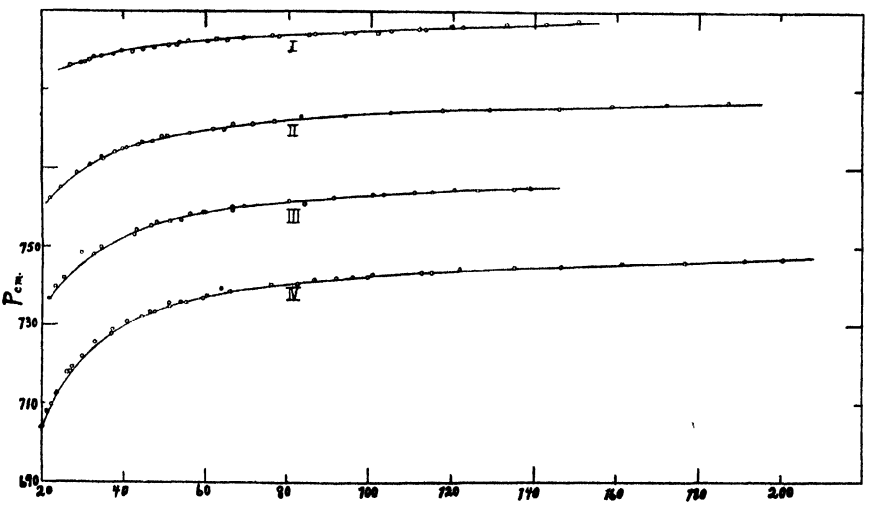
SERIES	MOLES NH_3 / MOLE NH_4Cl	P	SERIES	MOLES NH_3 / MOLE NH_4Cl	P
		cm. Hg			*cm.* Hg
A	2 06	314 0	D	13 8	725 9
B	2 38	314 9	C	16 0	729 0
B	2 62	364 3	D	17 9	730 7
B	2 90	421.2	E	20 0	732 4
B	3 10	456 5	D	24 9	735 2
B	3 37	497 8	D	32 0	737 6
A	3 67	530 3	D	34 7	738 6
B	3 90	558 2	E	51 3	741 7
B	4 32	595 8	F	60 7	742 5
A	4 89	629.0	G	69 0	743 4
A	6 21	674 5	F	86 4	744 2
C	6 71	685.6	G	105	745 2
C	7 48	696.5	F	111	745 5
C	8.55	707 0	G	122	745 9
A	9 41	712.4	G	133	746 8
B	9 96	714 0	G	143	747 1
C	12 2	722.3			



Moles NH_3/Mole Solute

FIG. 3. VAPOR PRESSURES OF SOLUTIONS IN THE CONCENTRATED REGION

I, ammonium chloride; II, ammonium bromide; III, ammonium nitrate; IV, ammonium iodide.



Moles NH_3/Mole Solute

FIG. 4. VAPOR PRESSURES OF SOLUTIONS IN THE DILUTE REGION

I, ammonium chloride; II, ammonium bromide; III, ammonium nitrate; IV, ammonium iodide. Curves I, II, and III have been displaced upward on the ordinate 60, 40, and 20 cm., respectively.

pressed in moles per mole of salt. The tables include only a fraction of the measured pressures.

DISCUSSION OF RESULTS

By this method it is impossible to carry the solutions to the desired dilutions so that we can calculate the activity of the solute. However, we are measuring the freezing points of the dilute solutions and will be able to furnish additional data in a subsequent article.

Since the dielectric constant of ammonia is low, one expects a low activity of the electrolytes in this solvent. However, because of the great proton accepting power of ammonia one expects these ammonia salts to have a high activity. Our vapor pressures indicate that the solute ions are associated in our most dilute measurements. The order of association is what is to be predicted from the magnitude of the ion diameters.

The extremely low concentration of H^+ or protons in (l) NH_3 leads the authors to avoid the term, acids in (l) NH_3, in the usual sense that the term acid is used.

SUMMARY

The vapor pressures of solutions of ammonium nitrate, ammonium chloride, ammonium bromide, and ammonium iodide in liquid ammonia have been determined over as wide a concentration range as possible at 25°C.

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RATES OF COAGULATION. I

AUTOCATALYSIS AND SOL PURITY

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Received November 17, 1933

In a series of studies involving the use of the photoelectric cell as a means of measuring rates of coagulation, Desai (1) and Desai and Patel (2) observed definite evidence of an induction period in the coagulation process. Since the extent of this induction period was found to decrease with increased purification of the sol employed, it seemed pertinent to repeat Desai's studies, using the presumably highly purified sols prepared in this laboratory (4, 5).

The light source used was a 300-watt "Champion" tungsten-filament bulb which was operated on 60 volts at 1.78 amperes. The light from this lamp, which was cooled by placing it in a water bath through which passed a copper coil containing running water, was passed through a lens ($f = 6$ cm.) placed at a distance equal to its focal length from the filament. In series with the lamp were a key, a variable 10-ohm resistance, and an ammeter which could be read to 0.01 ampere. The light, which could be shut off by a shutter placed directly in front of the lens, then passed through a metal tube set in a thermostat to an inner container in the thermostat. Here were placed, in order, a filter of a 2 per cent solution of copper nitrate contained in an optical glass absorption cell (10 × 100 × 100 mm.), the reaction cell (10 × 100 × 70 mm.), also of optical glass, and a photoelectric cell. This last was a product of the General Electric Company (P. J. 23) containing cesium as the sensitive material, which when operated on an anode potential of 90 volts delivered a maximum peak anode current of 5 microamperes.

This current was passed through a Leeds and Northrup wall galvanometer whose sensitivity was 1655 megohms. Readings of the galvanometer deflection were taken on a scale 2.5 meters along its arc, placed at a distance of 7 feet from the galvanometer mirror.

The source of current for the lamp was a bank of storage batteries whose output current was maintained at a constant value by means of the variable resistance mentioned above.

EXPERIMENTAL

Preliminary experiments showed that the ferric oxide sol which was used was not affected by light after an exposure of from three to four hours, and that pure electrolyte solutions were without appreciable effect on the

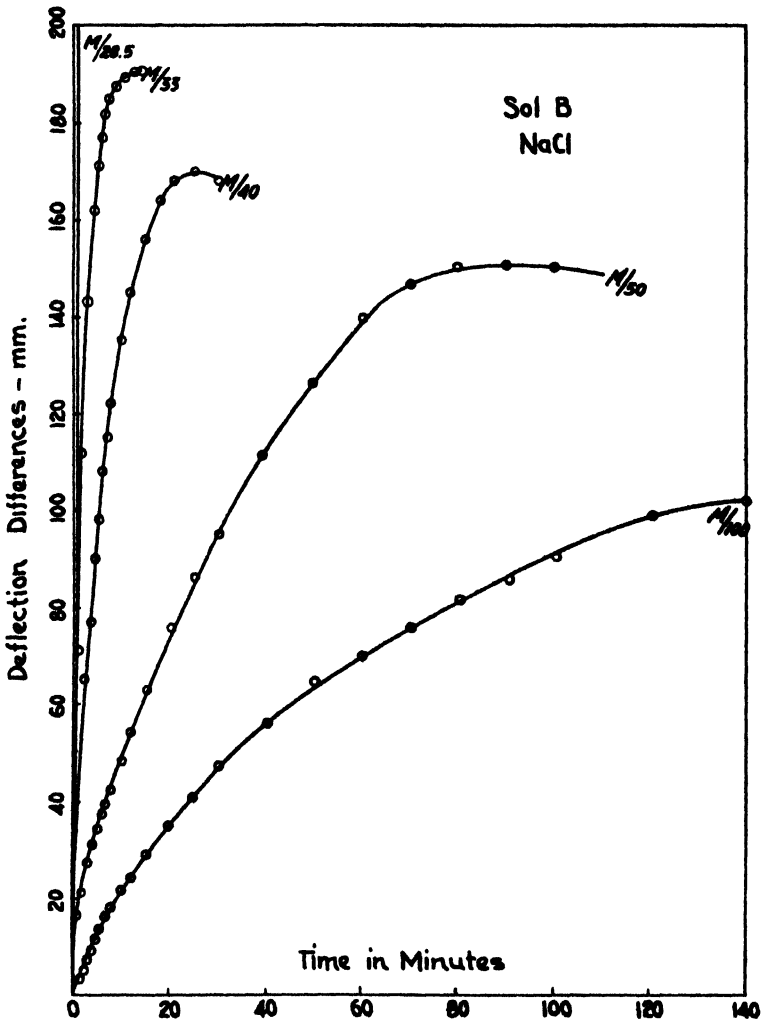

FIG. 1. COAGULATION RATES WITH SODIUM CHLORIDE

intensity of the transmitted light. Before each determination, a blank was run using 10 cc. of sol diluted with 20 cc. of distilled water in the reaction cell. The necessary time was allowed for all external conditions to become constant and the galvanometer reading was then taken. The zero point was obtained by cutting off the light with the shutter, and the

difference between these two values taken as the standard deflection for the sol under investigation as a measure of the opacity of the pure sol with no added electrolyte.

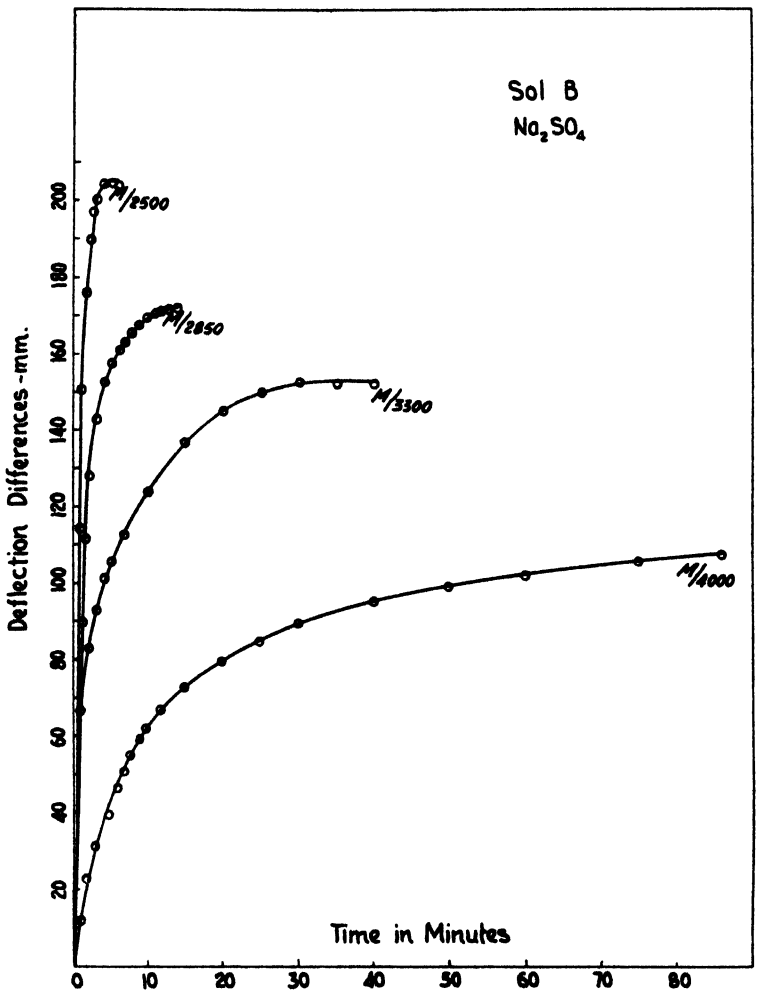

FIG. 2. COAGULATION RATES WITH SODIUM SULFATE

Twenty cc. of electrolyte was then placed in a 125-cc. Erlenmeyer flask, the time taken as being the zero time for the run, and 10 cc. of sol pipetted into the flask. The reaction mixture was then quickly transferred to the reaction cell and the cell placed in its proper position in the inner container of the thermostat. As nearly as possible, the same mixing technique was employed in every determination so as to eliminate any effect due to stirring.

At various times, readings were taken on the galvanometer scale and the differences from the standard deflection plotted against the time, giving the curves shown in figures 1 to 5.

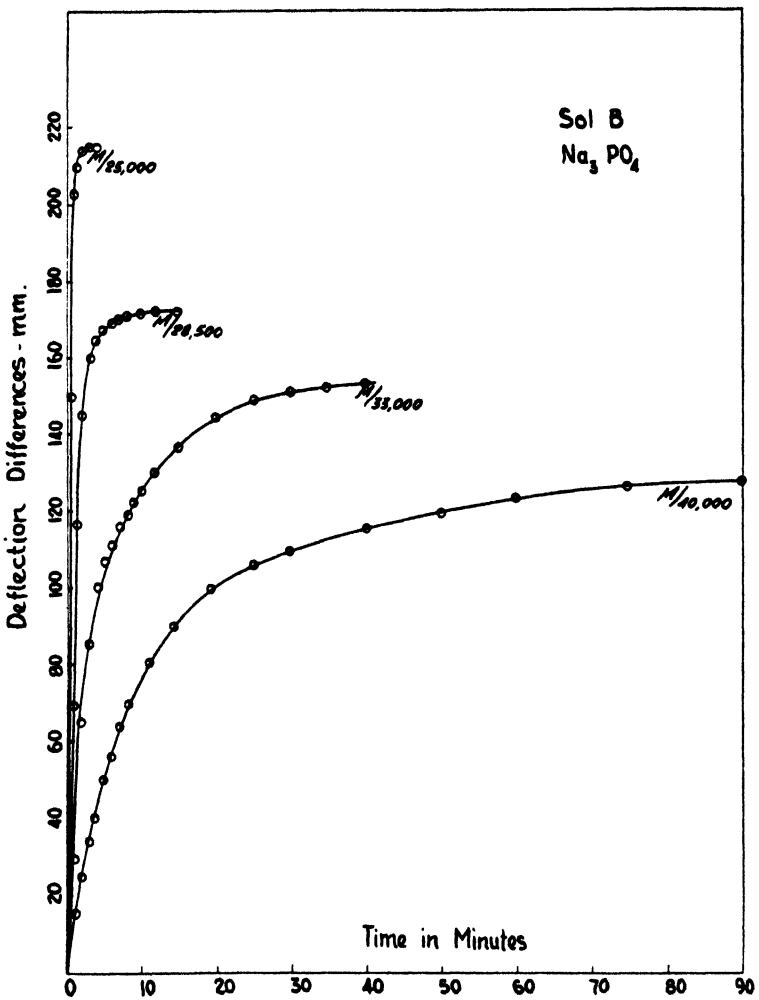

FIG. 3. COAGULATION RATES WITH SODIUM PHOSPHATE

DISCUSSION

Since the decrease in intensity of the transmitted light is a measure of the increase in flocculated sol, the slopes of the various curves give a direct measure of the rate of coagulation at any given time. The plotted results show no induction period; neither do they show any autocatalytic tendency (3).

In all curves there is an evident tendency for the rate to drop off toward the end. Since, in keeping with Desai's technique, the sol–electrolyte mixture was not stirred, this is no doubt caused by a counter-clarification due to sedimentation of the flocculated material. The actual appearance

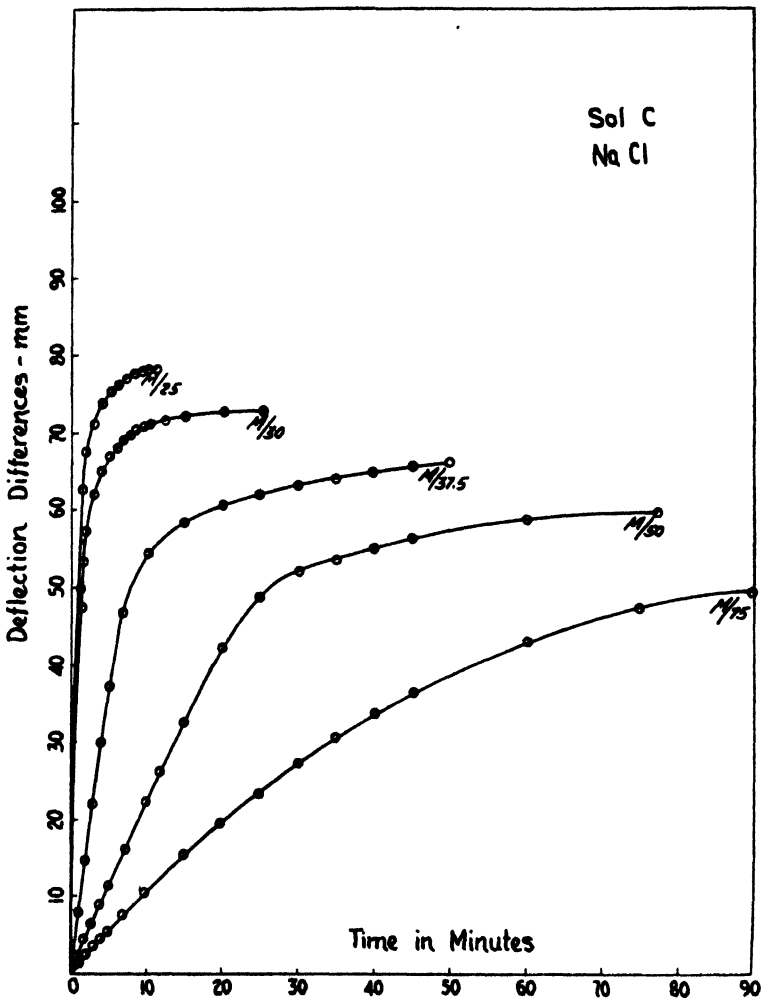

FIG. 4. COAGULATION RATES WITH SODIUM CHLORIDE

of a floc at the bottom of the cell, and the fact that this dropping off in the rate of decrease of intensity of the transmitted light was more pronounced when the beam of light was shot through the top of the cell and less pronounced when shot through the bottom substantiates this contention.

In view of the fact that agglomeration is presumably the result of colli-

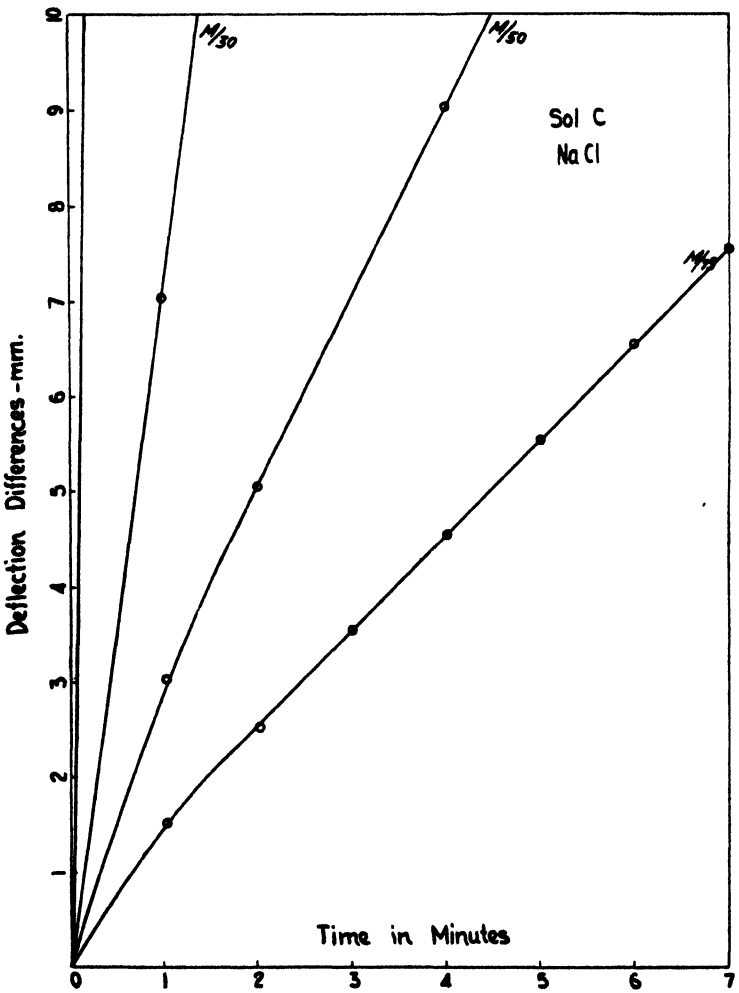

FIG. 5. COAGULATION RATES WITH SODIUM CHLORIDE

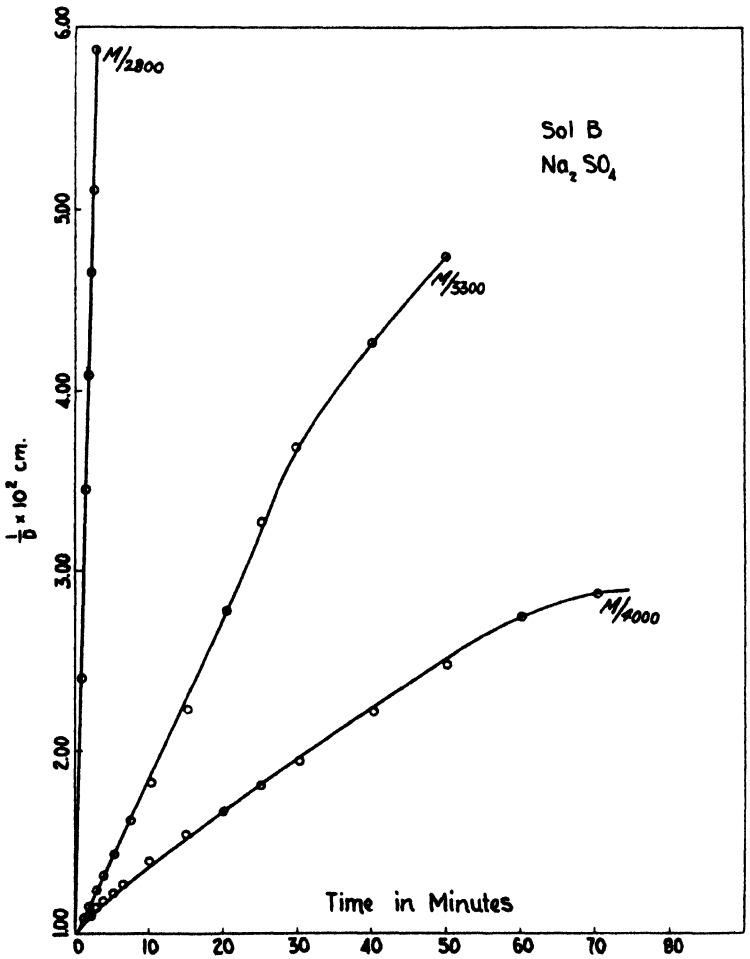

FIG. 6. ORDER OF THE COAGULATION PROCESS

sions between two or more particles, it is to be expected that the reaction might be of second order. In the event that it is second order a straight line should result if the reciprocal of the direct galvanometer reading, which reading is a direct measure of the concentration of unflocculated sol, is plotted against time. Such graphs are shown in figure 6. The results seem to warrant the conclusion that the coagulation process is essentially second order.

The results of studies with stirred sol–electrolyte mixtures will be presented in a later paper.

SUMMARY

1. The rate of coagulation of highly purified ferric oxide sols by various electrolytes has been studied by means of the photoelectric cell using the technique developed by Desai.

2. There is no evidence of an induction period in the flocculation process; the process does not appear to be autocatalytic. This is in agreement with a prediction contained in Desai's experimental results.

3. The flocculation process appears to be essentially of second order.

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(3) Mehta and Joseph: J. Indian Chem Soc. **10**, 177 (1933).
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THE TEMPERATURE COEFFICIENT OF PHOTOGRAPHIC SENSITIVITY. I

Low Temperatures and the Natural and Optical Sensitivities of Dyed Silver Halides[1]

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The primary object of the present study was to ascertain if the natural and the optical sensitivities of dye-sensitized silver halide were sharply differentiated as regards temperature influence. If this were not so, this would be evidence that the mechanism of latent image formation must be very similar in both cases. On the other hand, a very considerable difference, particularly at quite low temperatures, might strengthen the case for those who support a more or less complicated chemical reaction as the basis of optical sensitizing (14).

In discussing previous work on the subject of temperature influence, we regard it as desirable to deal separately, at least for the present, with investigations below normal temperature—i.e., below 20°C.—and those above. Since the experiments to be described in this first part deal with the lower range, discussion of relevant literature will be confined to this interval.

Much of the work on the effect of temperature on sensitivity appears to be rather discordant. Dewar and Abney (4), for example, reported a lowering of 80 per cent in "sensitivity" at −180°C. as compared with that at room temperature, whereas A. and L. Lumière (16) reported that it required 350 to 400 times more exposure to produce the same density on plates exposed at −191°C. as at room temperature, i.e., about 99.7 per cent loss.

Some have found only a slight (if any) change in sensitivity with increasing temperature (21, 22) from −50°C. to +100°C., and others a considerable increase (1, 3, 4, 12, 16, 18, 19, 23); some have even found a decrease at the higher temperatures (2, 13).

R. J. Wallace (29), plotting density (less fog) against temperature (from −20°C. to +100°C.), found that the lower densities (up to about 1.2) passed through a maximum between −20°C. and 0°C., and decreased more or less for higher temperatures.

[1] Contribution No. 528 from the Eastman Kodak Co.

The first to notice an effect of temperature on contrast (gamma, or gradation of density with exposure over the normal exposure region, for different development times) was Abney (1). He found that for the most part for exposures with time variation, i.e., intensity constant, temperature variation made little, if any, change on the contrast. With intensity varied and time held constant, he found a lowering of contrast with decrease of temperature between +34°C. and −15°C.

King (13) also mentioned the change of contrast with temperature, but did not say in which direction it trended.

Wallace (29) found that between −10°C. and +20°C. contrast decreased and above 20°C. it remained constant, under the conditions of his experiments. It should be remembered that his results represented sensitometric curves with fog subtracted uniformly for all densities.

Eggert and Luft (5) have tried to explain some of these discrepancies. They found that in plotting the dependence of density for constant energy of (white light) illumination, and (presumably) constant development time, against the temperature, the curve drawn through the observed points had a maximum between −60°C. and −20°C., and a minimum between +40°C. and +60°C., somewhat similar to those of Wallace but at different temperatures. Gammas for the same characteristic curves (for constant development time) from which the densities are taken, decrease to a minimum and then increase again. X-rays, however, produced only a small steady increase in density, for constant energy of illumination, with temperature increase.

One cause for the lack of agreement among the various investigators as to the effect of temperature change on photographic sensitivity has been the looseness with which the word "sensitivity" has been used. It has had distinctly different meanings with different workers. We shall use the term to imply the average relative sensitivity of all the silver halide grains of the plate, as modified by their surroundings of gelatin, etc., the relative sensitivity of the individual grains being defined as the exposure (to some standard light source) just sufficient to make the grain developable under some chosen standard conditions of development, which takes into account the developer, the temperature, and the time of development.

We shall use the term "speed" to mean $10 \times 1/i$, i being the inertia of the plate, or that exposure on the log E axis at which the straight-line portion of the D–log E curve extended cuts the axis. This is often called the H. and D. speed, although Hurter and Driffield used a different factor than 10.

Another cause for the discrepancies in conclusions concerning the effect of temperature lies in the fact that no two investigators used the same sensitometric procedure. The conclusions were derived from very meager

data, frequently from just two or three exposures and one development time, the conditions of exposure and development not being specified, nor the type of plate used.

Even more important, as indicated by recent unpublished investigations by Dr. J. H. Webb, of the Physics Department of this Laboratory, is the intensity level. Since our results were obtained with a mixed régime, i.e., an intensity scale of exposures instead of a time scale, they can only be regarded as comparative, but we regard them as significant for the comparison of natural and optical sensitivities.

This investigation is by no means complete, having been conducted so far at only three temperatures, −180°, −70° and +20°C., and with comparatively few different kinds of plates, but results have already been obtained which it was felt warranted publication.

EXPERIMENTAL PROCEDURE

The plates which were cooled to −70°C., and their controls at room temperature, were exposed in a vertical sensitometer in which they lay on a metal box, in a metal drawer. The temperature of the box was lowered by partly surrounding it with solid carbon dioxide, and by passing through it acetone cooled by allowing it to flow through a copper coil packed in solid carbon dioxide in a surrounding vessel. The system was well insulated, and was provided with a means of raising the acetone back from a lower reservoir into an upper reservoir after the latter had emptied itself.

The temperature at the surface of the plate was determined by pressing against it a calibrated alumel–chromel thermocouple, connected with a galvanometer and rheostat, the former having a scale graduated in tenths of a millivolt, and which could easily be estimated to 0.1 to 0.2 millivolt. The thermal junction was flattened so as to make as intimate contact with the plate as possible.

The calibration was carried out by burying the thermocouple in liquid nitrogen, liquid oxygen, solid alcohol, solid ethyl chloride, solid carbon dioxide, a soft mush of carbon dioxide in acetone, salt and ice in water, pure ice in water, and water at various temperatures above 0°C. up to 60°C.

As the room temperature was fairly constant, in the neighborhood of 20°C., the refinement of operating the above thermocouple against a standard at, say 20°C., was found unnecessary, although the room temperature was recorded.

A curve of the galvanometer readings plotted against temperature was drawn, and found to be practically a straight line above −80°C.

There was no appreciable condensation of moisture on the plate when placing it in the sensitometer nor during the period it remained there,

since practically all moisture inside the sensitometer was displaced by the rapidly evaporating carbon dioxide.

The same sensitometer was used for attaining exposures at −180°C., but the cooling system was modified, in that liquid air was passed directly from its upper container through an insulated tube to the metal box which was partly surrounded by either liquid air or liquid nitrogen, and from the metal box to a lower container, and the whole system was more thoroughly insulated.

The temperature of a plate lying on the metal box when the latter was surrounded with liquid nitrogen was very little, if any, different from that when liquid air was used as the surrounding medium, because liquid air was flowing rapidly through the inside of the box all the while.

The difference in speed and in contrast at −180°C. (noted below), when liquid nitrogen was used around the box in the drawer, as compared with liquid air, was therefore not due to temperature difference but perhaps to the presence of a small amount of ozone in the oxygen vaporized from the liquid air. The ozone would no doubt react with the dye in the panchromatic plate, which, it was observed, does very quickly lose its orchid color in the vapor above liquid air, even without the action of light. Dewar has shown that liquid air, when evaporating, does form some ozone, especially when acted on by light (4).

Because the rubber tube connections would become hard and brittle at that low temperature, the metal drawer containing the metal box was fastened securely to supports screwed to the work bench, and the sensitometer was put on a platform on wheels and rolled back and forth to open and close it.

The sensitometer itself (27) consisted of a balopticon with a short-focus lens, which focused, for the desired time, the image of a step tablet onto a 4 x 5 inch plate lying on the metal box in the metal drawer, by opening and closing a metal flap in front of the lens. The exposure time was either 1 minute or 2 minutes.

The light from the sensitometer lamp (which was operating at about 110 volts) before reaching the plate, passed through filters. With panchromatic plates, either a Wratten No. 39 glass filter + a 15 per cent copper sulfate solution in a 1-cm. deep glass cell, or a Wratten No. 9 + a Wratten No. 29 gelatin filter were used to give *blue-violet* or *red* light, respectively. The former combination has a maximum transmission at about 380 mμ to 400 mμ and no transmission of wavelengths longer than 510 mμ. The latter filters cut off all light of wavelength shorter than 600 mμ. With the process plates, not dye-sensitized, we substituted for the red filter a Kodak No. 4 filter, transmitting only beyond 480 mμ.

After the exposure at the low temperature, the plate was placed in a 4 x 5 inch plate box. Of course, some moisture condensed on it in trans-

TABLE 1

Comparison of relative speeds of panchromatic plates for blue-violet and red light at different temperatures with pyro–soda developer

	COLOR OF ILLUMINATION	TEMPERATURE	SPEEDS FOR DEVELOPMENT TIMES OF									AVERAGE SPEED
			2 min.	3 min.	4 min.	6 min.	10 min	15 min	20 min	30 min	60 min.	
		degrees C										
Control	Blue-violet	+20	479	417	417	417	417	417	417	(417)*	—	425
	Red	+20	324	324	324	324	324	324	324	(324)	—	324
Solid carbon dioxide	Blue-violet	−70	363	288	288	316	692	—	—	—	—	389
	Red	−70	229	229	229	263	331	—	—	—	—	256
Liquid nitrogen	Blue-violet	−180	39	39	39	39	50	(51)	(53)	55	23	43
	Red	−180	11	12	8 3	12	12	10	(10)	10	10	10 6
Liquid air†	Blue-violet	−180	22	25	25	25	28	28	(29)	30	—	27
	Red	−180	—	—	35‡	17	8 7	8 7	(8 7)	8 7	—	10 4

* Parentheses indicate interpolated or extrapolated values.

† Differences between liquid air and liquid nitrogen, which are particularly notable with panchromatic plates, are probably due to certain amounts of bleaching of dyes by ozone from the liquid air.

‡ These values not included in the averages.

TABLE 2

Comparison of relative speeds of panchromatic plates for blue-violet and red light at different temperatures using p-aminophenol developer

	COLOR OF ILLUMINATION	TEMPERATURE	SPEEDS FOR DEVELOPMENT TIMES OF								AVERAGE SPEED
			3 min	4 min	6 min	10 min	15 min	20 min	30 min	60 min	
		degrees C									
Control	Blue-violet	+20	562	513	339	339	309	309	(378)	447	400
	Red	+20	316	316	316	363	363	251	251	—	311
Liquid air	Blue-violet	−180	—	—	47 0	118	—	118	47 0	—	83
	Red	−180	—	—	17 4	17 4	—	17 4	(17 4)	—	17 4

ferring it to the box, but this, it was known from previous experiments on the effect of moisture on the sensitivity and latent image (27), had no appreciable effect on the latter. The plate was not developed until it had attained room temperature again and the moisture had evaporated.

The plate which had been cooled was developed along with an uncooled one which had previously been exposed in the sensitometer at room temperature (about 20°C.) (or in some cases with one which had been cooled after exposure) in a standard pyro–soda developer[2] at 20°C. Development time was varied from 2 minutes to 60 minutes. Some experiments were also done using *p*-aminophenol developer.[3]

EXPERIMENTAL RESULTS

The full results are best presented as the actual sets of characteristic curves obtained at each temperature and for all times of development,

TABLE 3

Comparison of relative speeds of process plates for blue-violet and bluish green-yellow light at different temperatures using pyro–soda developer

	COLOR OF ILLUMINATION	TEMPERATURE	SPEEDS FOR DEVELOPMENT TIMES OF		AVERAGE SPEED
			2 min	6 min	
		degrees			
Control	Blue-violet	+20	84	89	87
	Green-yellow	+20	11 5	12 6	12
Liquid nitrogen	Blue-violet	−180	5 3	3 4	4 4
	Green-yellow	−180	0 63	0 63	0.63

but this is likely to be regarded as taking too much space. We give, therefore, tables of sensitometric variables taken from these curves, as well as graphs derived from these. In tables 1 to 3 are given the data on total speeds[4] at 20°C., −70°C., and −180°C. for Wratten panchromatic

[2] Standard pyro–soda developer:

Solution A:

Na_2SO_3 (anhydrous)	256 g.
$NaHSO_3$	70 g.
Pyrogallol	80 g.
Water to	4 l.

Solution B:

Na_2CO_3 (anhydrous)	300 g.
KBr	4 g.
Water to	4 l.

[3] Standard *p*-aminophenol developer:

p-Aminophenol hydrochloride	7.275 g.
Na_2SO_3 (anhydrous)	50. g.
Na_2CO_3 (anhydrous)	50. g.
Water to	1. l.

[4] Not subtracting fog. For practical photographic purposes, "speed minus fog" or a similar value, is more useful, but not for sensitivity studies.

plates, with *blue-violet* and *red* radiation, respectively, with both a pyro-soda, and a *p*-aminophenol developer, as also the value of γ (gamma), the slope of the characteristic curve. Data are also given for a process plate for *blue-violet light* (maximum at 380 mμ to 400 mμ) and for bluish green-yellow rays longer than 480 mμ, of which only the shorter ones are effective. These represent data on wavelength effect *within* the natural absorption region of the silver iodobromide, and not for optically (dye) sensitized material.

TABLE 4

Wratten panchromatic plate

TEMPERATURE		SPEED NUMBERS					
		Blue-violet			Red		
Pyro-soda developer							
degrees C.							
20		425	≏ 100	per cent	324	≏ 100	per cent
−70		389	92		256	79	
−180	(Nitrogen)	43	10		10.6	3 5	
−180	(Air)	27	6 3		10 4	3 3	
p-Aminophenol developer							
20		400	≏ 100	per cent	311	≏ 100	per cent
−180	(Air)	83	20		17.4	5	
Process plate							
TEMPERATURE		<480 mμ			<480 mμ		
Pyro-soda developer							
degrees C.							
20		87	≏ 100	per cent	12	≏ 100	per cent
−180	(Nitrogen)	4 4	5		0 63	5	

The average values of the relative speeds are collected and reduced to a percentage basis in table 4. It will be noticed that while the fall in speed—and consequently in threshold sensitivity—is comparatively small from 20°C. to −70°C., it becomes very considerable, both for the natural and the optical sensitivity, from −70°C. to −180°C. The results for the Wratten panchromatic plates appear to indicate that the optical sensitivity ("red") falls off considerably more than the natural or blue-violet values. But this cannot be regarded as proven by these data, because

the values for the blue-violet sensitivity at −180°C. are rather widely scattered, namely as follows:

Panchromatic plates at −180°C

Pyro	Nitrogen	10.0 per cent of 20°C. speed (blue-violet)
Pyro	Air	6.3 per cent of 20°C. speed (blue-violet)
P. A. P.	Air	20.0 per cent of 20°C. speed (blue-violet)

Process plate

Pyro	Nitrogen	5 per cent of 20°C. speed

Also, there are no data on process plates cooled in the presence of liquid air or developed in *p*-aminophenol.

TABLE 5

Comparison of gammas of panchromatic plates for blue-violet and red light at different temperatures, with pyro-soda developer

	COLOR OF ILLUMINATION	TEMPERATURE	VALUES OF GAMMA FOR DEVELOPMENT TIMES OF							
			2 min	3 min	4 min	6 min	10 min	15 min	20 min	30 min
		degrees C								
Control	Blue-violet	+20	0.52	0.85	1.12	1.45	1.84	2.16	2.67	—
	Red	+20	0.64	1.09	1.53	2.08	3.10	3.72	4.00	—
Solid carbon dioxide	Blue-violet	−70	0.33	0.56	0.67	1.00	1.17	—	—	—
	Red	−70	0.40	0.66	0.81	1.15	1.68	—	—	—
Liquid nitrogen	Blue-violet	−180	0.15	0.28	0.42	0.68	1.07	1.30	—	1.85
	Red	−180	0.15	0.25	0.43	0.62	1.13	1.62	—	2.10
Liquid air	Blue-violet	−180	0.09	0.18	0.25	0.44	0.81	0.93	—	1.55
	Red	−180	—	0.06	0.17	0.27	0.63	0.84	—	1.37

Hence it does not appear possible to conclude that the optical sensitivity is much more depressed than the natural (blue-violet) sensitivity, in so far as threshold sensitivity is concerned.

A more definite distinction between the blue-violet and red light-exposed plates appears in regard to contrast (γ_∞) and perhaps maximum developable density (D_{max}) which would be an approximate measure of the total photographic "yield." The data (tables 5 to 8) indicate that for the blue-violet there is no considerable fall of γ_∞ or D_{max}, but chiefly a shift of inertia with lowered temperature. With the "red" light, however, there appears to be a progressive reduction of γ_∞, with possibly some fall of D_{max} (cf. table 8). If it were quite correct that there were no fall of γ_∞ with lowered temperature for "blue-violet" light (*i.e.*, with fall of

TABLE 6

Comparison of gammas of panchromatic plates for blue-violet and red light using p-aminophenol developer

	COLOR OF ILLUMINATION	TEMPERATURE	VALUES OF GAMMA FOR DEVELOPMENT TIMES OF							
			3 min	4 min	6 min	10 min	15 min	20 min	30 min	60 min
		degrees C								
Control	Blue-violet	+20	0 62	0 83	1 20	1 54	1 89	2 08	—	2 21
	Red	+20	1 01	1 46	1 74	2 56	2 83	3 06	3 90	—
Liquid air	Blue-violet	−180	—	—	0 25	0 31	—	0 54	0 75	—
	Red	−180	—	—	0 21	0 32	—	0 48	—	—

TABLE 7

Comparison of gammas of process plates for blue-violet and green-yellow light at different temperatures using pyro-soda developer

	COLOR OF ILLUMINATION	TEMPERATURE	VALUES OF GAMMA FOR DEVELOPMENT TIMES OF	
			2 Min	6 Min
		degrees C		
Control	Blue-violet	+20	1 67	3 48
	Green-yellow	+20	1 90	4 36
Liquid nitrogen	Blue	−180	0 37	1 51
	Green-yellow	−180	0 30	1 14

TABLE 8

γ_∞ for panchromatic plates at various temperatures with blue-violet and red light

COLOR OF LIGHT		γ_∞			
		At 20°C	At −70°	At −180° 1 *N.*	At −180° 1 a
Blue-violet	(a)	2 13	--	1 53	1 42
	(b)	2 52	1 56	2 72	2 67
	(c)	2 93	—	2 56	2 70
Red	(a)	4 49	—	2 17	1 13
	(b)	5 04	3 28	3 49	1 82
	(c)	4 46	—	2 61	1 26

(a) Values in this row determined from equation $d\gamma/dt = k(\gamma_\infty - \gamma)$ and intermediate values of gamma are approximately constant.

(b) Values in this row determined from the above equation with $\gamma = 0$.

(c) Values in this row determined from the above equation with γ for 30 minutes development time, except those at −70°C., which were obtained with γ for 10 minutes development time.

natural sensitivity) then the general results could be diagrammatically represented as in figure 1. This would mean that as regards "blue-violet" radiation, all grains, of whatever initial size and sensitivity, were equally reduced in sensitivity (causing a parallel shift in the characteristic curve).

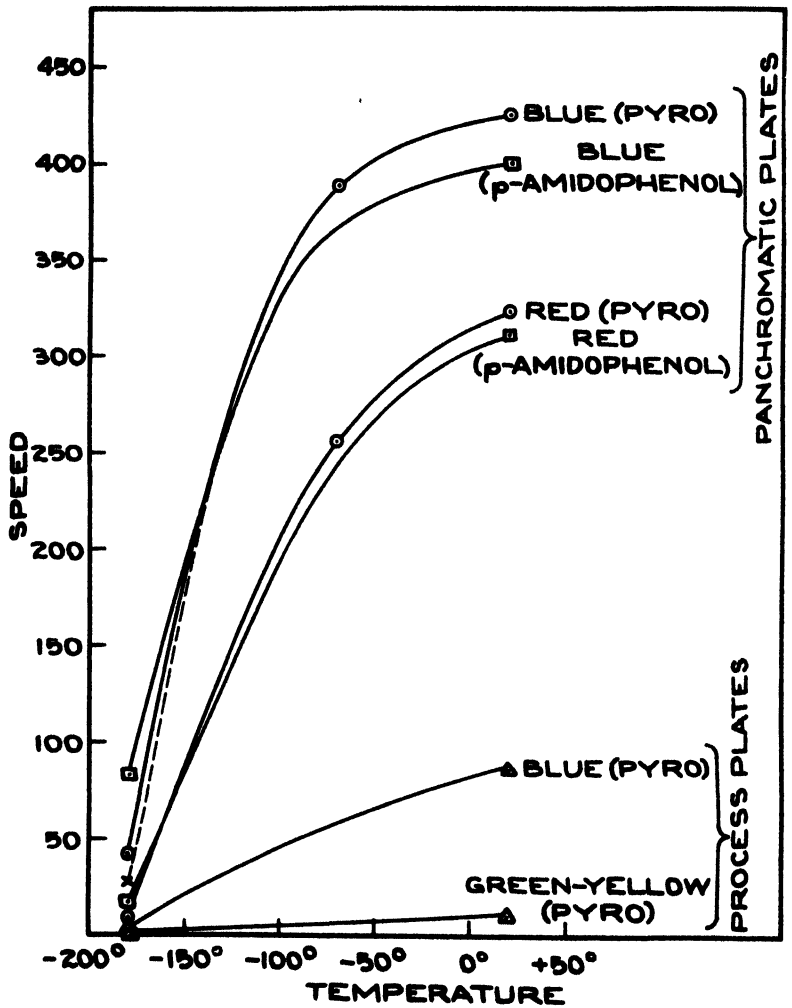

FIG. 1. EFFECT OF TEMPERATURE ON SPEED

There is some evidence against this in the somewhat larger speed reduction of the process (slower, fine-grained plate) than of the panchromatic plate. But the influence of "desensitization" on the temperature coefficient remains to be specifically investigated. Provisionally, all that one can say is that there seems to be less tendency to diminution of sensitivity

at very low temperatures for the natural (blue-violet) sensitivity than for the optical (dye) sensitivity, for the most sensitive grains, but that the changes in sensitivity become of the same order for the grains of lower sensitivity.

DISCUSSION

We may summarize the principal results of the investigation in the form of four propositions, and then consider possible interpretations of these.

1. There is a relatively small drop in sensitivity, both natural and optical, from 20°C. to −70°C.
2. There is a large drop in both cases from −70°C. to −180°C.
3. Even at −180°C. there persists some 5 per cent or more of the original threshold sensitivity at 20°C.
4. Latent image formation by red light in optically (dye) sensitized grains seems to be affected by very low temperatures similarly to the process in grains of low sensitivity with blue-violet light

Effect on absorption

According to Fesefeldt and Gyulai (7), to Fesefeldt (6), and to Hilsch and Pohl (11) the ultra-violet and violet absorption of silver chloride is very little affected, about 5 per cent by a temperature of −180°C. On the other hand, Toy and Harrison (28) give values for the absorption coefficients of silver bromide at −180°C. showing a much larger decrease in absorption, viz., about 75 per cent at 365 mμ, 59 per cent at 406.2 mμ, and 45 per cent at 435.8 mμ. Between 20°C. and −180°C. they found the decrease in direct proportion to the temperature drop.

Hilsch and Pohl (11) state that the absorption spectra of the color centers (produced by ultra-violet illumination) in silver chloride and silver bromide crystals were unaffected (within probable experimental error) by temperatures down to −180°C. *If* the absorption of silver bromide is more affected by temperature drop than that of silver chloride, it is possible that that of silver iodide would be still more seriously reduced, and even that of silver iodobromide more than that of pure silver bromide. However, the small effect of a temperature drop to −180°C. on the absorption of thallium bromide and thallium iodide observed by Fesefeldt (6) makes any such large changes as those given by Toy and Harrison seem doubtful. Hilsch and Pohl speak, in fact, in general terms of "the practical temperature independence of the absorption spectra of the silver halides." It may be doubted, therefore, whether change of absorption contributes materially to the fall of photographic sensitivity of the non-optically sensitized silver halide.

In the case of dye-sensitized material, it is the absorption of the ad-

sorbed dye which is in question. We have not found much information in the literature on the effect of low temperatures on the absorption by dyes, at least in the solid state, which is the nearest to that concerned. The investigations of Königsberger and Kilching (15) were concerned with temperatures from 20°C. upward. For dyes such as fuchsin, cyanin, iodeosin—sufficiently near in type to sensitizing dyes—they concluded: (1) that absorption in the visible spectrum is due to one resonating electron per molecule; and (2) that for a rise of 75°C. the maximum was displaced some 8 mμ toward the longer wavelengths, and only slightly weakened and broadened.

The inference would be that, as found with other materials, lowering the temperature to say −180°C., might displace the absorption maximum about 10 to 20 mμ toward the shorter wavelengths, and somewhat narrow the absorption band. On this basis, there appears no reason to expect so large a lowering of total red sensitivity as was actually found.

Primary and secondary processes

Regarding the primary process, in the case of the silver halide, as the absorption of light and, to a first approximation, as

$$\mathrm{Br}^- + h\nu \rightarrow \theta + \mathrm{Br}$$
$$\mathrm{Ag}^+ + \theta \rightarrow \mathrm{Ag}$$

the parallel event for the dye would be

$$D + h\nu \rightarrow \theta + D^1$$

where D^1 represents an unsaturated radical derived from the dye molecule, which can, for example, couple to form with another D_2, just as dianthracene is formed from anthracene on exposure to ultra-violet light[5] (17, 20).

$$\mathrm{A} + h\nu \rightarrow \theta + \mathrm{A}^1$$
$$\mathrm{A}^1 + \mathrm{A}^1 \rightarrow \mathrm{A}_2$$
$$\mathrm{Ag}^+ + \theta \rightarrow \mathrm{Ag}$$

Since neither of these photoelectronic processes would be much affected by temperature change, we must look for the carrier of the temperature effect in secondary processes of latent image formation:

1. In the case of ultra-violet and blue-violet sensitivity (natural absorption by silver halides) this might be a greater regression of latent

[5] The mechanism suggested for these photopolymerizations is that of an internal photoelectric effect. Both anthracene and the sensitive dyes show external photoelectric effects in the shorter ultra-violet, and the dyes (cf. A. Goldmann: Ann. Physik [4] **28**, 449 (1908)) give photovoltaic effects in aqueous systems for light in their visual absorption bands.

image after low temperature exposures, by bromine. Thus, conceivably at higher temperatures, the bromine atoms formed are very rapidly removed, whether by interaction with gelatin or other halogen acceptor. It is feasible that at very low temperatures, not merely is this reaction suspended, the bromine atoms being frozen in *statu nascendi*, but that on return to normal temperatures the bromine has a greater probability of attacking the latent image silver atoms. Certainly in one respect a difference would exist. Any bromination (or halogenation) occurring *in light* at normal temperatures would be partly a photobromination; such photobrominations have notoriously high temperature coefficients for photochemical reactions (8). In any event, the possibility exists that retarded halogen acceptance may account for the considerable fall of sensitivity of non-optically sensitized silver halide.

However, it appears more difficult to account in this way for the equal or greater fall in dye-induced optical sensitivity, since there is no evidence that in this case any halogen is actually liberated. It would require very complicated and rather improbable mechanisms to ensure that the light absorbed by the dye molecule should not only release an electron from a halide ion, but also, and necessarily, pass this on to a silver ion.

2. An alternative secondary process is that involved in aggregating or *concentrating* sufficient silver atoms produced by the primary process to form a nucleus capable of inducing development. On the orientation theory of "concentration specks" (25) it is supposed that silver sulfide specks in the grain induce or orient the reaction

$$Ag^+ + \theta \rightarrow Ag$$

to occur at the interface Ag_2S : Ag Hal. Whether the whole quantum event

$$Br^- + h\nu \rightarrow Br + \theta + Ag^+ \rightarrow Br + Ag$$

is thus oriented, or only the part reaction above, is not implied in the theory. An essential corollary to this is that as far as the natural absorption is concerned, the whole projective area of the grain is the receptive or working area (25). This has recently received confirmation from experiments by J. H. Webb on the reciprocity failure (30).

The studies on photoconductance in the silver halides by Toy and Harrison (28), and by Harrison (10), as well as those on the photovoltaic effect with silver:silver halide electrodes by Sheppard and Vanselow (26) indicate that the photoelectrons in silver halide crystals can traverse quite considerable distances. Gudden and Pohl (9) point out that this is characteristic of crystals with high refractive index, in which the potential barriers between adjacent ions are not so steep as those in purely ionic lattices, such as the alkali halides. In any case, the orientation

hypothesis presupposes a system of energy slopes, or potential gradients, in the crystal focusing upon the speck. It appears feasible that at very low temperatures this system is altered, that the lattice becomes more like that of the alkali halides, so that orientation of the photo-effect becomes increasingly difficult,—which would be equivalent to a progressive desensitization by reduction of receptive area.

The data on the effect of low temperatures on photoconductance (10, 28), are too variable to throw much light on this. They do show, however, that the thermal history of the crystal, and its consequent structure, greatly affect the temperature coefficient.

It seems possible that further insight into the nature of the sensitivity drop at very low temperatures may be obtained, e.g., by examining the effect for x-rays or α-particles. This is *independent* of sensitivity nuclei, and only determined by the projective area (24). Again, the temperature coefficient of chemically desensitized plates should be compared with that before desensitization. Work on these phases is under way.

Density measurements and much of the development in the work here reported was carried out by Mr. E. Huberth, to whom we wish to express our thanks.

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STUDIES ON GLASS. IX

THE ELECTRICAL CONDUCTIVITY OF BORON TRIOXIDE–SODIUM BORATE GLASSES[1]

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It has been shown quite conclusively that the conduction of an electric current by certain glasses is due to the transference of ions (5). In other glasses, however, such as those composed of very simple inorganic and complex organic molecules, it is difficult to decide on the nature of the charge carriers.

Schonborn has presented data on certain borosilicate glasses which conduct ionically (3). His measurements show a definite break in the conductivity–temperature curve at a point corresponding to the softening region of the glass.

With boron trioxide, however, no evidence of such a change in the transition region has been reported (4, 6). Various boron trioxide–sodium borate systems have also been measured, but these too showed no irregularities.

This investigation represents a further study on boron trioxide–sodium borate (B_2O_3–$Na_2B_4O_7$) systems, undertaken and carried out with the aid of a new and highly refined method of measurement.

APPARATUS AND PROCEDURE

The apparatus used to make the conductivity measurements was a modification of that described by Clark and Williams (1). The modifications were introduced in the interests of greater sensitivity and ease of control. The circuit was essentially a modified Wheatstone bridge employing precision standard resistances, variable potentials on two of the bridge arms, and a high-sensitivity quartz-suspension Compton electrometer.[3]

For measurements on pure boron trioxide and mixtures containing small percentages of sodium borate, a conductivity cell was constructed of Monel

[1] This work is a contribution to the series of studies on glass which are being conducted by Professor George S. Parks at Stanford University.

[2] Shell Research Fellow at Stanford University, 1932–1933.

[3] The refinements of the apparatus over that described by Clark and Williams (1) will be reported by one of us (J. D. C.) at a later time.

metal. The outside was turned to fit a cavity in a large electrically heated copper block. In the center of the Monel piece, a cylindrical cavity of 10.5 mm. diameter and 50 mm. depth was drilled. A piece of silver wire was connected with this container, which then served as one electrode. The other electrode was a Monel rod (6.80 mm. in diameter) extending through a hole in a copper plug which was turned to fit tightly in the cone top of the copper-block cavity. This electrode was insulated from the copper plug by means of two pieces of Pyrex tubing, one fitting inside the other, the Monel rod fitting inside the smaller one, and the outer one fitting into the hole drilled through the copper plug. The inner electrode was thereby concentric with the cavity in the container, leaving a space of 1.85 mm. between the two cylindrical surfaces.

The cell constant for the two concentric cylinders, neglecting the effect of the end surface of the rod,[4] is evaluated by the following equation:

$$\bar{\mu} = \mu \frac{\ln r_2/r_1}{2\pi L}$$

where $\bar{\mu}$ = specific conductivity, μ = reciprocal of measured resistance, and L = length of lateral exposure of the inner electrode.

For measurements on pure borax and mixtures containing high percentages of borax, the glass samples were blown in the form of tubes sealed at one end, having an outer diameter of about 1 cm. and an inner diameter of about 0.8 cm. The inner electrode consisted of a liquid sodium amalgam which was used as the anode. The tube containing the sodium amalgam was immersed in mercury, which served as the other electrode. A small electrically heated oven was used for temperature control. The cell constant was calculated in a manner similar to that above.

Temperatures were measured with a carefully calibrated noble-metal thermocouple and a White potentiometer. The thermocouple junction was inserted adjacent to the conductivity cell.

The samples of boron trioxide were prepared by heating in a platinum crucible at a temperature of 1200-1500°C. for one to two hours. The boron trioxide–sodium borate mixtures which were measured in the Monel cell were prepared by fusing the two components at the above temperature until all ebullition had ceased. While in a fluid condition, the sample was poured into the Monel container. The container was then heated to 600–700°C., placed in the copper block, and the inner electrode was immersed while the glass was still very hot. The system was brought to thermal balance at about 350°C. and measurements started at that point. The sample was then heated and cooled repeatedly over the temperature interval studied.

[4] A thickness of material between the end surface and the outer electrode was used such that a consideration of this effect is not necessary.

The glass tubes were prepared by heating and blowing to the desired shape.

EXPERIMENTAL RESULTS

Two samples of boron trioxide glass were first measured from 370°C. down to 130°C. Next, three boron trioxide glasses diluted with sodium borate were measured over a similar temperature interval using the Monel cell. The percentages of sodium borate present were 2.68, 5.42, and 16.74. As a check on the consistency of the procedure, another pure boron trioxide sample was measured at this point. Finally, pure sodium borate and 55

TABLE 1

Conductivity of a sodium borate–boron trioxide mixture

Per cent of $Na_2B_4O_7$ = 5.42

TEMPERATURE	RECIPROCAL OF MEASURED RESISTANCE	SPECIFIC CONDUCTIVITY
degrees C.	*ohm*$^{-1}$	*ohm*$^{-1}$ *cm*
353.1	8.84×10^{-9}	3.71×10^{-10}
346.0	5.68×10^{-9}	2.39×10^{-10}
344.8	5.05×10^{-9}	2.12×10^{-10}
333.4	2.15×10^{-9}	9.05×10^{-11}
324.2	1.15×10^{-9}	4.84×10^{-11}
310.5	3.42×10^{-10}	1.44×10^{-11}
306.3	3.10×10^{-10}	1.30×10^{-11}
296.0	1.70×10^{-10}	7.14×10^{-12}
289.0	9.50×10^{-11}	3.98×10^{-12}
265.7	2.14×10^{-11}	8.99×10^{-13}
264.3	2.42×10^{-11}	1.01×10^{-13}
260.6	2.08×10^{-11}	8.74×10^{-13}
244.5	1.39×10^{-11}	5.84×10^{-13}
229.0	7.69×10^{-12}	3.23×10^{-13}
211.8	4.30×10^{-12}	1.80×10^{-13}
194.8	2.46×10^{-12}	1.03×10^{-13}

per cent sodium borate glasses were investigated, using a sodium amalgam electrode and the small tubes prepared from the glass samples. These last two glasses were not studied at high temperatures because of vaporization of electrodes.

Each of the three pure boron trioxide glasses studied gave conductivity values in good agreement with the others. Plotting log of the specific conductivity (as calculated after evaluation of the cell constant) against reciprocal of the absolute temperature, straight lines over the measured temperature interval were found in every case. The accurate evaluation of the cell constant was rather difficult, and owing to this fact the curves for the three samples were parallel but not identical. The deviations were

small and can be attributed without question to the evaluation of the cell constant.

In table 1 the recorded data on one of the three mixtures are given. Smooth curves drawn through the recorded points are shown in figure 1. The curve for pure boron trioxide represents an average of the three samples measured.

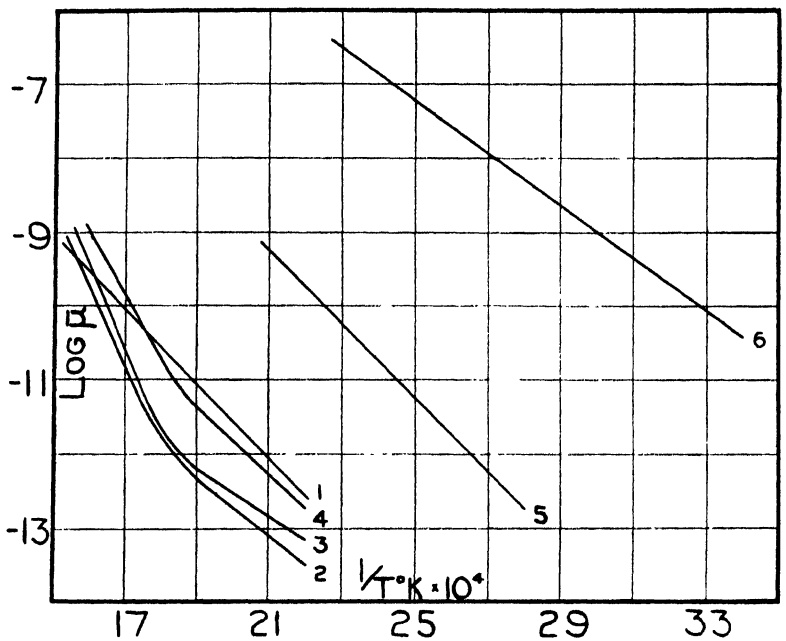

FIG. 1. SPECIFIC CONDUCTIVITY OF BORON TRIOXIDE-SODIUM BORATE GLASSES

1, Pure boron trioxide; 2, mixed glass containing 2.68 per cent sodium borate; 3, mixed glass containing 5.42 per cent sodium borate; 4, mixed glass containing 16.74 per cent sodium borate; 5, mixed glass containing 55 per cent sodium borate; 6, pure sodium borate.

DISCUSSION

The series of curves shown in figure 1 present two marked features: (1) In all cases of mixed glasses which were measured to about 250°C., a decided and rather sharp break was found in the conductivity curve. This break occurred in each of the three glasses measured in this temperature range at a point near the transition region of boron trioxide as determined from other physical data. (2) The addition of a small percentage of sodium borate to boron trioxide lowers the conductivity of the glass in the region of softening. As we go to higher temperatures, however, the mixed glass increases in conductivity more rapidly with temperature than

does the pure boron trioxide, and at high temperatures the mixtures are more conductive than the pure oxide.

Neither of the previous investigators of these systems has reported the abrupt changes in the direction of the conductivity curves of the mixed glasses in the transition region. Nevertheless, the data reported by Thomas (6) are in fair agreement with those presented here, especially at the higher temperatures. His values for boron trioxide–sodium borate mixtures show that at low temperatures the specific conductivities would be less than that of pure boron trioxide. Schönborn's investigations on borosilicate glasses (3) show conductivity curves which are of the exact nature of the mixture curves in figure 1.

The significance of the marked change of direction of the mixture curves is to be related to the gradual change in state of a glass in its transition region (2). It is known that a viscous liquid changes to a solid glass in a short temperature interval, and that many physical properties change in this interval with an abruptness that is suggestive of a crystallization process. The conductivity behavior of the mixed glasses seems to be further evidence of this change of state within a narrow temperature interval.

The addition of sodium borate to boron trioxide introduces sodium ions, and thereby evidently brings about ionic conductivity. When a glass conducts a current ionically, a break in the conductivity curve represents a change in the binding forces acting on the conducting ions. This might be expected in every case where the conducting ions are part of the molecules or aggregates composing the glass. If conduction is electronic, or due to foreign ions which are not affected by the glass structure, the transition of a glass to a viscous liquid would not necessarily affect the conductivity. In the case at hand, the presence of sodium ions in the mixtures introduces ionic conductivity, and a change in the direction of the conductivity curves might well be expected in the transition region.

Extrapolating the straight portions of the curves for the mixtures, points are obtained which can be considered as the "transition temperatures" of the glasses. For the three mixtures containing low percentages of borax, these values are 271°C., 279°C., and 276°C., named in the order of increasing sodium borate content. The transition temperature for pure boron trioxide, as chosen from other physical data, is in the neighborhood of 250°C. (6).

The straight unbroken curve for pure boron trioxide suggests that the conduction is not carried on by ions which are part of the glass structure. Many oxides have been found to conduct electronically, and this is probably the nature of the conduction by this substance.

The decrease in conductivity when sodium borate is added to boron trioxide seems to indicate that the addition of ionic conductors disturbs

the inherent ability of the boron trioxide to conduct electronically. As the percentage of sodium borate increases, however, the ionic conduction becomes greater, and apparently surpasses that of pure boron trioxide as higher percentages are reached. Even with small amounts of sodium borate (2 to 5 per cent), the ionic conductivity increases so rapidly with temperature that in the neighborhood of 350°C. the conductivity exceeds that of pure boron trioxide. Below the hardening region the curves are approximately parallel.

Although direct current was used in the measurements, polarization effects were not noticeable in the samples containing small percentages of sodium borate. If conduction by pure boron trioxide is electronic, no polarization would be expected in any case.

The glasses containing a high percentage of borax were measured with a sodium amalgam anode which acted as a source of sodium ions and thus prevented polarization. An attempt was made to measure these samples with the Monel cell, but polarization effects were evident. However, measurements were made on the 16.7 per cent sodium borate sample using the amalgam anode, and results were obtained which were in very close agreement with those obtained using the Monel cell. This fact shows that with glasses containing low percentages of sodium borate, polarization is unimportant.

SUMMARY

The electrical conductivities of boron trioxide, sodium borate, and some boron trioxide sodium borate systems have been measured over a 240° interval with a modified Wheatstone bridge method.

Pure boron trioxide shows a smooth even conductivity curve over the entire measured range, but the mixed glasses gave fairly sharp breaks in the curves in the region of transition of the glasses. These breaks are considered to be associated with the changes in many physical properties in the interval where a viscous liquid changes to a hard glass.

The addition of small percentages of sodium borate to pure boron trioxide causes the conductivity to decrease, but further addition causes a steady increase.

It is our pleasure to express appreciation to Professor George S. Parks and Dr. F. O. Koenig of this department for their help and advice in this work.

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A STUDY OF THE ADSORPTION AT THE BENZENE-SODIUM OLEATE SOLUTION INTERFACE

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Since Langmuir (11, 12) and Harkins (4) first suggested that an oriented monomolecular layer of adsorbed material existed at the interface of emulsions, considerable experimental work has been done to test the validity of their suggestion. The results obtained are conflicting; some show adsorption equivalent to a monomolecular film, while others give evidence of films of greater thickness.

Griffin (2) attempted to confirm the theory with a study of emulsions of kerosene with solutions of sodium oleate and stearate. He found approximately a monomolecular layer. Van der Meulen and Riemann (17, 18) reported similar results with toluene emulsified with solutions of sodium ricinoleate and sodium oleate. In the latter case phenol was added to the toluene used in preparing the emulsions. Undoubtedly phenol or sodium phenolate was adsorbed at the interface in addition to the sodium oleate. Since the interfacial areas were calculated statistically by these workers from relatively small amounts of material the results are somewhat uncertain.

Studies by McBain and his coworkers (13, 14) on the adsorption of such substances as *p*-toluidine, amyl alcohol, nonylic acid, phenol, etc., at the interface between the aqueous solution and nitrogen gas have repeatedly shown the formation of films more than one molecule thick. With sodium oleate solutions and nitrogen bubbles, Laing, McBain, and Harrison (10) found sufficient adsorption for a dimolecular layer.

Nonaka (20), using a Donnan pipet, studied the adsorption of sodium oleate and palmitate on droplets of toluene and found greater than monomolecular adsorption.

Harkins and Beeman (3) made measurements on emulsions containing a much greater number of droplets than those of Griffin and of van der Meulen and Riemann. Using emulsions of various oleates and octane they failed to find adsorption more than sufficient to form monomolecular films. Harkins and Fischer (5), in examining sodium oleate-paraffin oil emulsions, measured the size of 1000 to 3000 droplets in each emulsion

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studied and computed from these results the distribution of size and the total interfacial area involved. The adsorption found was only sufficient to form a monomolecular film.

All the studies, except those of Nonaka, on the liquid–liquid interface in emulsions of oils with dilute soap solutions have been made by preparing an emulsion in the usual manner and then attempting to estimate the total interfacial area by statistical studies of the size distribution of the droplets. The distribution of the fatty acid between the two phases was permitted to take place during and after emulsification. The measurements on such systems involve approximations which necessitate considerable experimental error. The writers surmise, too, that with the close packing of the oil droplets in such an emulsion, some of the adsorbed material might be squeezed out into the excess of dispersion medium. There is much need for work that is more quantitative and affords more uniform conditions at the interface.

The work presented in this paper is a study of the adsorption of sodium oleate at a water–benzene interface, using droplets of benzene of uniform size. The experimental set-up was similar to that used by McBain and his coworkers (10, 13, 14) in their study of adsorption at a nitrogen gas–aqueous solution interface. This type of apparatus has not been used before with systems having liquid–liquid interfaces. The number and size of the droplets were known, which permitted a quite accurate estimate of the area of the interface. Benzene and sodium oleate solutions were chosen as the two phases, because this system is easily reproducible and has been widely used, thus permitting a greater comparison with the work of other investigators. The experiments differ further from previous work in that the two phases were brought to equilibrium prior to making the adsorption measurements in all but one experiment. In such a system the fatty acid formed by the hydrolysis of the sodium oleate distributes itself between the two phases.

EXPERIMENTAL

Materials

The benzene used was of "C. P. analyzed" quality. It was redistilled and only the middle portion boiling over a one-degree range was used.

Eimer and Amend's "C. P. linolic acid-free" oleic acid, also used by Harkins and Fischer (5), was found to be a very pure product. This acid was used throughout and proved to be very uniform in quality.

The soap was prepared in two ways. That used in the first two experiments was prepared from sodium ethylate and oleic acid in the method developed by Harkins and Beeman (3). Solutions prepared from this soap tended to become turbid, probably owing to the presence of acid soap. In

order to avoid this difficulty and any possible contamination from carbonate, the soap solution used in the subsequent experiments was made directly in the 5-liter flask in which the two phases were later allowed to come to equilibrium. The carbon dioxide-free base used in preparing the solution was made (7) by dissolving stick sodium hydroxide, "C. P. from alcohol," in distilled water to form a saturated solution. This was centrifuged and the supernatant liquid used to prepare a concentrated stock solution. It was stored in a paraffined bottle and standardized for later use.

In preparing the soap solution the required amount of the stock sodium hydroxide solution was carefully pipetted into the 5-liter flask. Oleic acid in slightly less amount than that equivalent to the base was then added to the solution and the mixture heated under a reflux condenser until saponification was complete. After cooling, the soap solution was diluted with freshly boiled distilled water until the solution weighed approximately 2250 g. A solution of a weighed quantity of oleic acid in approximately 2500 cc. of benzene was next prepared. The amount of oleic acid was such that if it were added to an equal volume of the soap solution the concentration of the excess sodium hydroxide would still be at least 0.001 *N*.

After the foam which formed on the soap solution during the dilution had disappeared, the benzene solution was added. By running the benzene in with extreme care, the emulsion formed at the interface occupied only a few per cent of the total surface. The weight of the benzene solution added was such that the two phases had an equal volume.

The flask was then placed in a thermostat at 25°C. and the two phases allowed to come to equilibrium. Placing a portion of the oleic acid in the benzene phase greatly shortened the time required to reach equilibrium, since the upward diffusion, into the benzene, of the oleic acid formed by hydrolysis of neutral sodium oleate is very slow. The downward diffusion was hastened by cautiously rotating a bent stirring rod in one phase and then in the other.

Preliminary tests showed that equilibrium was attained in ten days to two weeks as a maximum. This was determined by removing, at intervals, a sample of the benzene phase and determining the concentration of oleic acid. When no further decrease in the acid content could be detected after five days standing, it was assumed that the solutions were at equilibrium.

To provide for rapid attainment of equilibrium in the first two experiments, in which pure solid soap was used to prepare the solutions, a small quantity of oleic acid was added to the benzene and slightly more than an equivalent amount of carbon dioxide-free sodium hydroxide was added to the soap solution.

Although the alkali added in preparing the soap solution used in experi-

ment No. 1 was in excess of the oleic acid added to the benzene phase, the solution never became clear. The solid soap must have contained some free fatty acid or, more probably, some acid soap. Undoubtedly this solution, which showed considerable turbidity, contained a larger amount of colloidal material than would have been found in a clear solution of this dilution.

When it was desired to use the solutions, they were removed from the flask by siphoning into separate bottles. The soap phase was placed in a Pyrex bottle. Care was taken at all times to avoid contamination by carbon dioxide. The bottles were stored in the thermostat and both phases were analyzed as described below.

As a check on the other experiments, experiment No. 7 was made with a soap solution which was not at equilibrium with the benzene phase. The soap solution was prepared to duplicate the materials used in experiment No. 6 as closely as possible. That is, since pure benzene was used, the soap solution was made not only so that it contained very nearly the same normality of sodium as the solution used in experiment No. 6, but also so that it had approximately the oleic acid content which would have resulted if all the oleic acid in a given volume of the benzene used in No. 6 were transferred to an equal volume of the soap solution for No. 6.

Analytical

Owing to the large size of the benzene droplets used in the experiments and the resulting low specific interfacial area (total area in square centimeters / total volume in cubic centimeters of the benzene), the amount of material adsorbed, if a monomolecular layer were formed, was too small to obtain sufficiently accurate results by the volumetric determination of the oleic acid. It was thought that the sodium could be determined with sufficient accuracy by titration. The solutions used in the first two experiments were analyzed in this manner, but satisfactory results were difficult to obtain and in the later experiments the analyses were made entirely by gravimetric methods as described below.

Analysis of the equilibrium benzene solution. Approximately 10 cc. of the benzene solution was weighed into a tared weighing bottle. The benzene was then evaporated under reduced pressure in an oven at 50–55°C. After cooling, the oleic acid was weighed on a Kuhlmann microbalance. Weights were rounded off to five decimal places in grams. Two blanks were run with each set of analyses. A quantity of pure oleic acid approximately equal to that in the sample being analyzed was weighed into tared bottles and 10 cc. of pure benzene were added. The evaporation of the benzene, subsequent cooling, and weighing of the blanks and samples were carried out simultaneously. The weighed samples of oleic acid, used as blanks, usually showed an increase of a few hundredths of a milligram,

probably due to a slight oxidation of the acid while in the oven, although little air came into contact with the bottles during evaporation, since the benzene vapor was carried off by the suction. This increase in weight was used as a correction in the determination of the oleic acid in the sample.

From the weight of the sample and the weight of the oleic acid, the concentration in milligrams of oleic per gram of benzene was calculated. The weighings in all analytical work reported in this paper were corrected to weight in vacuo.

Checks on carefully prepared standard solutions of oleic acid in benzene showed that the estimation of the acid by microgravimetric means was far more accurate than by titration with standard aqueous or alcoholic sodium hydroxide. In fact, considerable time was lost in unsuccessful attempts to titrate the oleic acid according to the methods used by previous investigators.

Analysis of equilibrium soap solutions. For this analysis special tubes of Pyrex glass were prepared by sealing a piece of tubing 1 cm. in diameter and 8 cm. in length to a test tube 2 cm. in diameter and 22 cm. in length. A sample of the equilibrium soap solution was placed in the tared tube and weighed. An excess of dilute sulfuric acid solution was then added, weighed, and finally 10 to 12 cc. of pure benzene saturated with water was added and weighed. The tube was sealed off and placed in a horizontal position in a slow rocker. After several hours the oleic acid was completely extracted by the benzene, both phases becoming clear. The neck of the tube was next cut off and a sample of the benzene solution was pipetted into a tared bottle and weighed. The benzene was evaporated as described above and the oleic acid weighed on the microbalance. Weighing bottles containing the proper weight of oleic acid were used as blanks. This procedure afforded the necessary data for the calculation of the concentration of oleic acid per gram of the soap solution.

This method was checked by analysis of a prepared standard soap solution 0.01522 N_w (weight normality), with the following results. Theoretical: 4.298 mg. oleic acid per gram of soap solution. Found. 4.295 mg. per gram.

In the first two experiments standard acid was added to the soap in the extraction tubes and the sodium was determined by titrating the excess acid with standard alkali. Difficulties in obtaining check results led to the use of the following method. A sample of the aqueous phase remaining in the extraction tube after the removal of the benzene was weighed into a tared platinum crucible. The water was evaporated in the oven by the same method as described for the benzene. The sodium sulfate was ignited in a muffle to constant weight and weighed to five decimal places in grams on the Kuhlmann balance.

Apparatus and procedure for carrying out an experiment. The apparatus

was a modified form of the one used by Laing, McBain, and Harrison (10) and is shown in figure 1. A and B are reservoirs for the equilibrium benzene solution. This arrangement was used in order to maintain a constant head of solution in B. Tube M connected bulb B to a gas washing bottle used to saturate the incoming air with benzene vapor. Stopcock C permitted regulation of the flow of benzene solution through the tip E. This tip was made by a careful thickening of a length of small Pyrex tubing and drawing it out to the proper diameter. The orifice was circular and the end was ground smooth. Preliminary work showed that the tip should be of a size to produce a benzene droplet approximately 2 mm. in diameter.

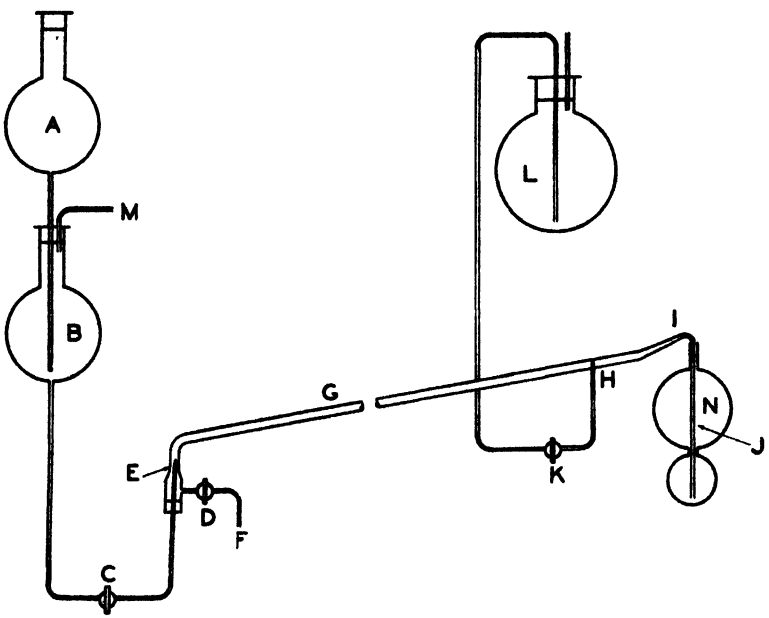

FIG. 1. ADSORPTION APPARATUS

With larger spheres the volume of benzene needed to form a sufficient number of droplets would be too great. Smaller droplets were very difficult to count accurately when the benzene flow was rapid enough to complete the run in a reasonable time.

Benzene droplets of this size did not appear to be deformed in any way during the passage through the adsorption tube and over the bend I, and in our calculations we have considered them to be perfect spheres.

L is the reservoir for the equilibrium soap solution. The tube H, through which the soap solution entered the adsorption tube G, projects about two-thirds of the way across the tube G, since preliminary work showed this was necessary in order to prevent the solution simply running

down the bottom wall of G and out the tube F without appreciably mixing with the solution in the tube. Tube G was approximately 100 cm. long, with an inside bore of 1 cm., and a volume of about 75 cc.

This tube made an angle of about 10° with the horizontal except for the last three centimeters before the bend at I. Here the slope was slightly steeper, and the tube was narrowed down until at the top of the bend the diameter was between 2 and 2.5 mm. The change in slope was small, as it was found that when the tube was steeper than 15° to 20° the benzene droplets jammed together and lost their spherical shape. The slight change in slope at the end of the tube served to separate any groups that formed as the droplets travelled up the tube.

The actual time each droplet was in the tube varied in the different runs from seventy seconds to nearly two minutes. This was much longer than the time the nitrogen bubbles used by Laing, McBain, and Harrison (10) and by Harkins and Gans (6) remained in the adsorption tube.

The collection flasks used were made by sealing a 100-cc. round bottom flask to the bottom of a similar 300-cc. flask (N, figure 1). Then the neck of the large flask was drawn out and a piece of tubing a few centimeters long and 1 cm. in diameter was sealed to it.

Before each experiment the entire apparatus was carefully cleaned with potassium dichromate–sulfuric acid cleaning solution, thoroughly rinsed with distilled water, and dried.

In making a run the apparatus was filled and the benzene flow adjusted so that about three droplets were formed per second. Then the stopcock D was regulated to allow between 100 and 200 cc. of soap solution to flow out during the run. Since the size of the drops from tube D varied with the concentration of the soap, and since it was found very unsatisfactory to make other than the small adjustments necessary to keep the run going smoothly after the start of the experiment, the amount of soap used as back current fluctuated considerably over the range 100 to 200 cc. per run. This was found sufficient, however, to prevent changes in concentration of the soap in the adsorption tube.

Finally, the flow of soap solution into the apparatus was so regulated that the droplets of benzene did not pack as they passed over the bend at I, and yet the excess of soap solution accompanying them was kept as low as possible.

Since the benzene droplets could not be carried up a steep tube and thereby drained of the excess of soap solution, as was done by Laing, McBain, and Harrison (10) with nitrogen bubbles, the solution in the receiving flask was only slightly more concentrated than that in the adsorption tube. This factor combined with the low specific interfacial area makes the determination of the actual adsorption one requiring very carefully executed technique.

When all the adjustments were properly made the weighed collection flask was saturated with benzene vapor, pushed up on the tube J, and lightly stoppered to prevent evaporation of benzene vapor. The time of placing the flask in position was recorded and the length of the run was accurately timed. Every five minutes during the course of the run the speed of formation of droplets was measured. This was done by noting, with the aid of a stopwatch, the time required for fifty droplets to pass a given point on the tube. From these readings, and the time elapsed during the run, the total number of droplets was computed. From the weight and density of the benzene collected the volume and the surface of the droplets were calculated.

The temperature of the room was held very constant during the course of a run. At rare intervals and then only for a few minutes at a time did the temperature vary more than ± 0.5°C. from 25°C.

Except for the first two experiments, duplicate runs were made consecutively with no break in time. In the first two experiments only one run was made in a day and the check run was made the following day.

After completion of a run the analytical procedure described above was immediately carried out. The data of the experiments are given in table 1.

Determination of weights of materials used and calculations of results. Previous to placing flask N in position its weight (W_E) was carefully determined to ± 2 mg. At the completion of the run the weight (W_T) of the flask plus the solutions was found. Then a quantity of sulfuric acid was added in excess of that necessary to react with the sodium present. The flask was again weighed (W_A) and sealed.

By shaking the flask from time to time the oleic acid was extracted from the soap solution by the benzene. When extraction was complete the flask was opened and the greater portion of the benzene phase transferred by a siphon to a glass-stoppered bottle. The residue of the benzene was removed with a pipet and the upper bulb rinsed with petroleum ether. The last traces of the ether were driven out with a gentle stream of air, which was saturated with water vapor in order to prevent evaporation of the aqueous phase. After the removal of the benzene, the weight (W_U) of the flask and aqueous solution was determined.

The benzene layer was analyzed for oleic acid and the aqueous phase for sodium in the manner described above.

From these data the weights of the solutions used were found as follows: $W_T - W_E = W_R$, total weight of solutions used in the run. $W_A - W_W = W_{BO}$, weight of benzene solution plus oleic acid from soap solution. $W_R - W_{BO} = W_S$, weight of soap solution used minus its oleic acid. The weight of the oleic acid (W_O) removed from the soap solution by extraction can be found from the analysis of equilibrium soap and W_S. Then $W_S + W_O = W_{SU}$, weight of soap solution used. $W_{BO} - W_O = W_B$, weight of benzene solution used in forming droplets.

TABLE 1

Adsorption at the benzene–sodium oleate solution interface

	EXPERIMENT NO											
	I		II		IV		VI		VII		VIII	
	A	B	B	C	A	B	C	D	A	B	A	B
Oleic acid concentration, pre-run*	8 12	8 12	22 63	22 63	80 28	80 28	47.49	47 49	50 74	50 74	91 08	91.08
Sodium concentration, pre-run†	11 13	11 13	25 59	25 59	83 27	83 27	51.65	51 65	52 37	52.37	99 50	99 50
Oleic acid concentration, benzene‡	4 95	4 95	2 46	2 46	16 97	16 97	3.61	3 61	0 00	0 00	1 34	1.34
Excess sodium concentration§	3 01	3 01	2.96	2 96	2 99	2 99	2 16	2 16	1 63	1 63	8 42	8.42
Sodium concentration after run¶	11 23	11 22	25 80	25 80	83 78	83 85	51 88	51.80	52 57	52 79	100 25	100.52
Aqueous phase used (grams)	96 9	113.8	98 4	92 6	67 3	62 4	65 44	74 04	66 07	65 90	56 05	53.65
Benzene solution used (grams)	293 7	278 6	264 5	234 1	176 0	181 2	221 3	239 4	253.0	252.6	184 9	191 7
Total number of droplets $\times 10^{-3}$	60 50	59 80	61 50	64 40	60 00	61 40	48 30	49 00	41.10	41.50	50.30	50.00
Rate droplets per second**	2.71	3 06	3.10	3 12	4 17	4.27	3 35	3 40	3.42	3 46	3.50	3 47
Mean diameter droplets (mm.)	2.20	2.17	2 11	2 00	1 86	1 86	2.16	2 20	2 38	2 37	2 01	2 04
Oleic acid gain (mg.)	59 9	53 0	26 4	24 8	41 8	43 4	47 9	50 9	40 3	44 3	40 4	47 8
Sodium gain (equivalents) $\times 10^{6}$	9 694	10.24	20 3	19 5	35.0	36.0	13.74	8 88	13.2	27 6	42.0	54.7
"Layers" from oleic acid††	28 8	26 5	13.6	13 6	28 4	28 7	30 0	30.1	24 1	26 7	28.4	32 6
"Layers" from sodium‡‡	1.3	1 4	2 9	3 0	6 7	6.7	2 5	1 5	2 3	4 7	8.5	10 5
Specific interfacial area§§	27 2	27 6	28.4	30 0	31 4	32 2	27 8	27 3	25 2	25 3	29 5	29.4
Total time of run (minutes)	365	325	330	340	240	240	240	240	200	200	240	240

* Normality of equilibrium soap solution times 10^3. All concentrations for aqueous phases are given in weight normality.

† N_w aqueous phase times 10^3.

‡ Equilibrium benzene solution normality times 10^3. Volume normality calculated from weight analysis and specific gravity.

§ Sodium excess in equilibrium soap solution, $N_w \times 10^3$.

¶ $N_w \times 10^3$.

** Mean rate of formation of droplets during the run.

†† Number of monomolecular films equivalent to oleic acid gain.

‡‡ Number of monomolecular films equivalent to sodium gain.

§§ Total surface of droplets in square centimeters divided by total volume of benzene used in cubic centimeters.

Letting C represent the concentration (milligrams of oleic acid per gram of solution) of the solutions whose subscripts are used, we find the total gain in oleic acid as follows: $W_{BO}C_{BO} - W_{B}C_{B} - W_{S}C_{S}$ = mg. of oleic acid total gain.

The computation of the sodium gain was somewhat simpler. The difference between the normality of the sodium concentration in the equilibrium soap solution and the normality found for the soap solution collected gave the change in normality. This value multiplied by the number of cubic centimeters of soap solution carried over during the run and divided by 1000 gave the gain in equivalents of sodium.

The formulas for comparing the results obtained in these experiments with the gains which would have been required for monomolecular layers were derived as follows: Let M equal the weight in grams of benzene solution used, N the total number of benzene droplets formed, and G the milligrams of oleic acid gained during the run. The density of the benzene solutions used was equal to 0.873. The surface of a sphere is equal to 12.57 $\frac{(v)^{\frac{2}{3}}}{(4.189)}$, where v is the volume. Other constants used are: 6.06×10^{23}, Avogadro's number; 282.3, the equivalent weight of oleic acid; and 20.6 Å.,[2] the mean cross-section (1) of a fatty acid molecule.

From these values the following formula was derived:

$$\text{"Layer"} = \frac{(20.6)[(4.189)(0.873)]^{2/3}\ (6\ 06)\ 10^{7}G}{(12.57)(1000)(282.3)(M^{2}N)^{1/3}}$$

This reduces to:

$$\text{"Layers"} = \frac{(835.4)G}{(M^{2}N)^{1/3}}$$

This formula was modified to use with sodium gains, since by the method of calculation the gains were in equivalents. Using G in equivalents and multiplying the above formula by 1000 and 282.3, it becomes:

$$\text{"Layers"} = \frac{2.358 \times 10^{6}G}{(M^{2}N)^{1/3}}$$

It should be understood that the calculation of gain in "layers" is purely for the purpose of comparison with the amount necessary for the production of a monomolecular layer, and does not mean that the authors conceive of any such phenomenon as twenty or thirty layers of films at the interface.

RESULTS AND DISCUSSION

The results obtained were rather striking. In no case did the adsorption, as calculated from the gain in oleic acid, approach a monomolecular film.

In fact, with the one exception of experiment No. 2, the gain was more than twenty times that sufficient to form a film one molecule deep.

The adsorption calculated from the gain in sodium was much less. Though we found no adsorption so small as a monomolecular layer, three runs gave values less than sufficient for a dimolecular film, and in only four runs were the gains greater than five times that for a single layer of molecules.

A consideration of the experimental errors in analytical results and in counting the droplets showed that should all possible errors be cumulative they would not exceed 5 per cent of the amount of adsorption. It should be pointed out that there are several factors which, while probably negligible, would tend to make our results low rather than high. Though there was very slight drainage of the droplets it is possible that some of the adsorbed material could be brushed away from the surface in the adsorption tube. Another possibility is that oleic acid might be adsorbed from the benzene to the interface. Such an adsorption would not be shown by our procedure.

It is somewhat difficult to find a completely satisfactory explanation of the cause for this great difference in the amount of adsorption as measured by the gains found in the two constituents of the soap solution. A careful consideration of the results of other workers on the problem of adsorption of soap at the oil–solution interface, as well as of the studies made on the structure of the particles of sodium oleate in solution, brings out considerable suggestive material.

Laing (9) and Laing, McBain, and Harrison (10) have demonstrated the adsorption of acid soap at a nitrogen–sodium oleate solution interface. They reported a mean ratio of oleic acid to sodium of 1.70, which would account for an acid soap of the composition NaOl · 0.77 HOl.

Nickerson and Serex (19) studied the conductance of sodium oleate solutions in contact with benzene with results from which they conclude: "More acid sodium oleate is adsorbed at the oil–solution interface than at the vapor–solution interface," and "the rôle of acid sodium oleate has been much underrated."

Adsorption of the simple acid soap molecules, while undoubtedly a factor in the experiments we have made, would hardly account for the large ratio found between the gain in oleic acid and sodium in some of the runs.

From the results of experiments on the adsorption of sodium oleate and sodium palmitate at benzene and toluene interfaces, Nonaka (20) reached the conclusion that the adsorption of both soaps was of monomicellar rather than monomolecular order. He conceives of the micelle as consisting of the combination of the fatty acid micelle and neutral soap micelle in a tangled state. Later cataphoretic studies, in which Nonaka (21) used the same materials, led him to believe that the surface active material of the soap solutions must be the ionic micelle in all cases.

Thiessen and Spychalski (22) and Thiessen and Trubel (23) have made careful examination of the structure of sodium oleate in solutions by means of x-ray and double refraction studies, and conclude that the same micelles exist in solution as in gels (see also McBain and McBain (16)). These micelles Thiessen finds are rod-like, with the long chain of the fatty acid lying at right angles to the long axis of the rod. Two of the long faces of the micelles are made up of the carboxyl end of the soap. Thus in a neutral soap these faces would present a solid array of sodium atoms. If the micelle is not neutral some of the sodium atoms would be replaced by hydrogen. If micelles of this form should be adsorbed, the oleic acid gain would be much greater than that of the sodium.

Most of the work on the presence of micelles in soap solutions has been done at higher temperatures or at higher concentrations than we have used. However, in their determination of the micelle content of solutions of sodium oleate by means of ultrafiltration, McBain and Jenkins (15) worked with more dilute solutions and at 18°C. They could find no micelles in a 0.01 *N* solution, but using a 0.144 *N* solution the filtrate was only 0.001 *N*, indicating that nearly all of the material was of a colloidal nature. In discussing this work McBain says, "The 0.01 *N* solutions were filtered immediately after being prepared. It is possible that the colloidal acid soap formed by hydrolysis had not yet agglomerated sufficiently to be held back."

Later work by Laing (8, 9) in McBain's laboratory has afforded convincing evidence of the presence of ionic micelles in sodium oleate solution as dilute as 0.01 *N*.

The work alluded to indicates the probable presence of large molecular aggregates in sodium oleate solutions. It is not inconsistent to expect that such aggregates should be adsorbed at the benzene-solution interface. Such adsorption is in accord with the findings reported herein.

SUMMARY

1. An analytical method has been devised which is more accurate than the customary method of determining oleic acid.

2. A study has been made of the adsorption of sodium oleate at the benzene–sodium oleate solution interface. The adsorption found, as calculated from the gain in oleic acid, was, with the exception of experiment No. 2, equivalent to that necessary to form from twenty to thirty monomolecular films. The adsorption, as calculated from the sodium gain, varied from that nearly small enough for a monomolecular layer to that sufficient for ten such films.

3. Experiments have been made using solutions at equilibrium as well as non-equilibrium solutions. Similar results were found in both cases.

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NEW BOOKS

Elementary Quantitative Analysis. Theory and Practice. By HOBART H. WILLARD and N. HOWELL FURMAN. 14 x 22 cm.; viii + 406 pp. New York City; D. Van Nostrand Co., Inc., 1933. Price: $3.25.

This book by two of America's leading contributors to analytical chemistry presents more than enough theoretical and practical material for two semesters of work. Thus teachers are enabled to choose their determinations judiciously according to the samples available for analysis and the interests and aptitudes of their students. Although there has been a tendency in recent years to teach analytical chemistry mainly for the purpose of illustrating certain principles of physical chemistry, this text not only gives a thorough presentation of theoretical derivations and interpretations, but also describes an unusually large number of analytical determinations with that patient attention to detail which is essential for the successful guidance of beginning students.

The introduction of many new methods presents analysis as a living, growing branch of chemistry. The theory of adsorption indicators is carefully explained, and the Fajans method for chlorine in a soluble chloride is described in adequate detail. Although some recent texts make little or no mention of internal indicators for use with standard solutions of oxidizing agents, the authors have discussed these carefully and have described the use of sodium diphenylaminesulfonate in the bichromate method for iron. There is also an excellent section on ceriometry, which is based largely on the authors' own researches.

An interesting innovation in gravimetric analysis is the addition of urea to a solution from which calcium is to be precipitated with ammonium oxalate. Because of the hydrolysis of the urea into carbon dioxide and ammonia and the consequent slow neutralization of the slightly acidified solution, the calcium oxalate comes down in a very coarse form.

The solutions of many typical problems and the thought-provoking questions will be a great aid to both student and instructor. On pp. 272–3 two methods are given for calculating the results of indirect analyses. The second of these is by far the better. Because of the large errors involved in indirect analyses, very little space has been devoted to calculations of this type. The detailed discussions of the interfering substances and errors involved in each method and the various applications of each procedure are especially valuable.

Because of the wide scope of the book and its frequent references to the original literature, many thoughtful students will wish to keep it for their permanent libraries. Experienced analysts, also, will find in it many helpful suggestions.

MARY ELVIRA WEEKS.

Physical Constants, Selected for Students. By W. H. J. CHILDS. 17 x 10 cm.; viii + 77 pp. London: Methuen & Co., 1934. Price: 2s. 6d.

The dimensions of this small book, one of the publisher's series of monographs on physical subjects, comply with the intention of the author to present useful lists and tables in a form compact enough to go easily into the pocket.

The data chosen, under the headings General, Heat, Light, Magnetism and Electricity, and Sound, will be found useful to the physicist. A somewhat different

selection of material is needed to be of most use for the physical chemist, e.g., the replacement of astronomical and geodetical data by a more extended list of melting and boiling points and more information on definite chemical compounds. Units are defined, but only one calorie is mentioned. Conversion factors are few; there is none for electrical energy to heat. The data given for the surface tension of salt solutions imply that the latter is proportional to concentration.

At the end a list of general constants is given and mathematical tables which include four figure logarithms.

A pleasing feature of the book is the inclusion of seven nomographs which are practicable even within the small compass which the size of the pages allows.

W. H. PATTERSON.

Physico-chemical Methods. By J. REILLY and W. N. RAE. Second edition, revised. New York: D. Van Nostrand Co.

In the comparatively brief time since the first edition appeared, this book has become widely known and generally accepted as a reference book of physico-chemical methods. The second edition has been enlarged by the addition of new subject matter (twenty new chapters), and to some extent by the revision of the entire book.

The general revision still leaves something to be desired, since in a number of instances no reference is made to recent improvements of standard methods. For example, the use of butyl phthalate in condensation pumps is not mentioned. No reference is made to circulating pumps of the all-glass electromagnetic type. The extremely practical sensitive quartz spiral manometer of Bodenstein and Dux is not mentioned, although several other manometric devices of rather doubtful utility are described in detail. The Dennis melting point apparatus is not referred to. It is unfortunate that the chapter on photometry was written before the copper—cupric oxide (photronic) type of photoelectric cell came into general use.

The chapter on rates of reaction is not, in the opinion of the reviewer, up to the standard set by the rest of the book. This chapter consists of a brief discussion of the elementary theory of rates of reaction followed by detailed descriptions of seven experiments. The chapter would be much more useful if the space were devoted to a critical survey of methods available for measuring rates of reaction.

There can be no doubt, that, in spite of minor weaknesses, this book is an improvement on the excellent first edition. It is a highly practical book and will undoubtedly prove a time saver to many research students and investigators.

ROBERT S. LIVINGSTON.

The Kinetics of Reactions in Solution. By E. A. MOELWYN-HUGHES. Oxford: Oxford Press, 1933.

In this book the author attempts the difficult task of summarizing the more important data on the kinetics of chemical reactions in liquid systems and of coördinating this data in terms of the results of statistical mechanical analysis. Special emphasis is laid upon the experimental results which are in agreement with the predictions of the simple theory; and various explanations are advanced to demonstrate that the cases which are apparently not in agreement with the simple theory are not incompatible with it.

As is probably unavoidable in a work of this sort, the chapters are not of equal value. Three of the most original and valuable chapters are those dealing with the comparison of the kinetics of reactions in gaseous phase and in solution, with bimolecular reactions, and with unimolecular reactions. The chapter on equilibria seems unnecessarily involved, possibly because the activity concept is not intro-

duced earlier in the chapter. The discussion of complex reactions, in the chapter on ionic reactions, is somewhat disappointing. The discussion of enzyme reactions, in the chapter on heterogeneous reactions, while brief, is both interesting and stimulating. The bibliographies given are extensive enough to be useful, but in many cases are far from complete. To the reviewer there appears to be some bias in favor of articles which have appeared in English journals.

No student of physical chemistry who is interested in any phase of the kinetics of chemical reactions in liquid systems can afford to ignore this book. It should also prove very useful to organic chemists, biochemists, and others who utilize reaction velocity measurements in the study of their own problems.

ROBERT S. LIVINGSTON.

The Kinetics of Chemical Change in Gaseous Systems. By C. N. HINSHELWOOD. Third edition. 390 pp. Oxford Press, 1933. Price: $5.00.

Since the appearance of the first edition of this book in 1926 (second in 1929) notable advances have been made in the field of chemical kinetics of gases, to which the author has been an outstanding contributor. The present treatise is not only modern and authoritative but presented with unusual clarity.

One new chapter has been added, "Homogeneous Catalysis of Gaseous Reactions," which affords a very natural transition to some considerations of reactions in solution. Much new material has been added throughout which brings the work abreast of the present status of gas kinetics. The work will continue to be indispensable to all those interested in this field.

S. C. LIND.

Elementare Einführung in die Quantenmechanik. By K. K. DARROW. Translated from the English by E. Rabinowitsch. 22 x 15 cm.: 123 pp. Leipzig: S. Hirzel, 1933. Price: 6 RM.

Dr. Darrow, of the Bell Telephone Company's laboratories, is already well-known as a writer of unusual clarity and grace of style on many subjects of modern physics. In particular his "Electrical Phenomena in Gases" stands out as one of the very few comprehensive treatises on this subject. The present book follows naturally on the author's "Elementare Einführung in die Wellenmechanik" and forms the third volume in a series of books on new problems of physics and chemistry. The book is divided into two main parts, the first of which discusses the wave and corpuscular nature of matter and radiation, the wave equation, and the uncertainty principle of Heisenberg. These sections particularly are to be commended for their lucidity. Part II deals with the main subject matter of the book, quantum mechanics and the emission and absorption of light by atoms. The elementary principles of matrix algebra are considered and the author goes on to discuss the calculation of *eigen*-values by the matrix method and to demonstrate the connection between the wave mechanical and matrix treatment of atomic problems. As the title indicates, the whole is set out with the minimum of mathematical elaboration consistent with the thesis. The book should form an admirable introduction to one of the fundamental aspects of modern physics. Although originally written in English it has not, so far, been published in that language. All students of physics and chemistry who can read simple straightforward German are certain to derive benefit from this little book.

J. T. RANDALL.

Ueber heterogene Gleichgewichte chemischer Stoffe in Wissenschaft, Natur und Technik By ERNST JÄNECKE. 25 x 16 cm., 31 pp. Stuttgart: Ferdinand Enke, 1934. Price: 2.70 RM.

In this brochure, published in the well-known "Ahrens'sche Sammlung," now edited by Professor Grossmann, one of the foremost workers in the domain of heterogeneous equilibria gives a rapid survey of the principles of the phase rule as applied to systems of 1 to 5 components, with special reference to systems which are of importance in nature and in industry. The exposition, although necessarily brief, is clear and is made all the more easy to follow by the excellent diagrams which accompany the text. Advanced students will find this an excellent summary of some of the more important applications of the phase rule.

ALEX. FINDLAY.

Physica (Volume I, No. 1, December, 1933). 24 x 16 cm.; 96 pp. The Hague: Martinus Nijhoff. To be published in monthly parts, at a price not exceeding 25 guilders for the volume of 960 pages each year.

This new periodical takes over part of the title of *Physica, Nederlandsch Tijdschrift voor Natuurkunde*, which has been appearing since 1921. The *Tijdschrift* is to continue publication in Dutch, but the new *Physica* will contain, in English, French, or German, all original contributions to physics of the Dutch centers of research, and will serve also as a continuation of the *Archives Néerlandaises des Sciences Exactes et Naturelles.*

The introduction of a new periodical will be received with, at best, mixed feelings by all institutions working under strictly limited library allocations. An earlier circular from The Hague points out, however, that the contributions of Dutch physicists will no longer appear in the accustomed foreign, mainly German, periodicals; as the latter are generally sold by weight, it is argued that the advent of *Physica* will therefore involve no net increase in world expenditure on periodicals. There is incontrovertible logic in this, but the average illogical laboratory dweller will not easily be convinced, and it is only too likely that the members of his library committee will share his doubts.

The inevitable protest against any new periodical, *as such*, being discharged, it remains to review this latest example on its merits. The first number contains eight papers, covering a wide range of topics: adiabatic cooling of paramagnetic salts in magnetic fields (de Haas, Wiersma, and Kramers); concentration of Na atoms and Na^+ ions in the sodium low-voltage arc (Druyvesteyn); emission of light in gas discharges (de Groot); design of quartz-fluorite achromat (van Heel); dipole measurements with very small quantities of material (Henriquez); relative abundance of Li^7 and Li^6 isotopes (Ornstein, Vreeswijk, and Wolfsohn); photographic sum rule (van Kreveld); and Tchebycheff polynomials (van der Pol and Weyers).

Detailed discussion of these would be out of place here, but it may be said at once that the new periodical will rank as an important physical journal, with an appeal to a proportion of physical chemists as well as to all physicists. It has a distinguished editorial board, representative of the seven great research institutions of the Netherlands, on which it will rely for its articles. In view of the quantity and quality the work now issuing in an unbroken stream from these sources, *Physica* seen assured of success from the outset.

H. R. ROBINSON.

A THIRD ORDER IONIC REACTION WITHOUT APPRECIABLE SALT EFFECT

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Received November 24, 1933

A kinetic investigation (7), under the simplest experimental conditions, of the reaction

$$H_2O_2 + 3I^- + 2H^+ = 2H_2O + I_3^- \tag{1}$$

has confirmed the rate law

$$d(I_3^-)/dt = k_1^0\,(H_2O_2)\,(I^-) + k_1(H_2O_2)\,(I^-)\,(H^+) \tag{2}$$ [1]

previously discovered, and usually explained by assuming that the two rate-determining steps

$$H_2O_2 + I^- \xrightarrow{k_1^0} H_2O + IO^- \tag{3}$$

$$H_2O_2 + I^- + H^+ \xrightarrow{k_1} H_2O + HIO \tag{4}$$

proceed simultaneously and independently. Within the ionic strength range investigated (μ_c = 0.05 to 0.5), reaction 4 was concluded to be without appreciable salt effect, a conclusion so unusual for reactions involving more than one ion that another investigation was undertaken to test it; confirmation thereof is, we believe, furnished by the results that are to be presented here.

If (H_2O_2) is so small that (H^+) and (I^-) remain sensibly unchanged as reaction 1 proceeds, equation 2 may be written

$$d(I_3^-)/dt = k'(H_2O_2) = [k_1^0(I^-) + k_1(I^-)\,(H^+)]\,(H_2O_2) \tag{2a}$$

and k' may be evaluated as though it were the specific rate of a first-order reaction. Values obtained by measuring the rate at which I_3^- appears in reaction mixtures differing initially only in acid concentration may be plotted against (H^+), as in figure 1; when divided by (I^-), the slope of the resulting straight line gives directly the value of k_1, and the intercept similarly yields that of k_1^0. From one such series of reaction mixtures to

[1] At 25°C., k_1^0 = 0.69 at low ionic strengths, and k_1 = 10.5. ( ) will be used to denote "concentration of" in moles per liter. → will be restricted to reactions that may be rate-determining. Throughout, the minute constitutes unit time.

another, the ionic strength may be altered by the addition of some salt, e.g., sodium perchlorate; k_1^0 and k_1 may thus be obtained at different ionic strengths. Such measurements have been made; the results thereof are given in tables 1 and 2, and plotted in figures 1 and 2.

For sodium or barium perchlorate in moderate amount as added salt, these data show that the first term in equation 2, involving k_1^0, varies linearly with the ionic strength, while the second, involving k_1, is independ-

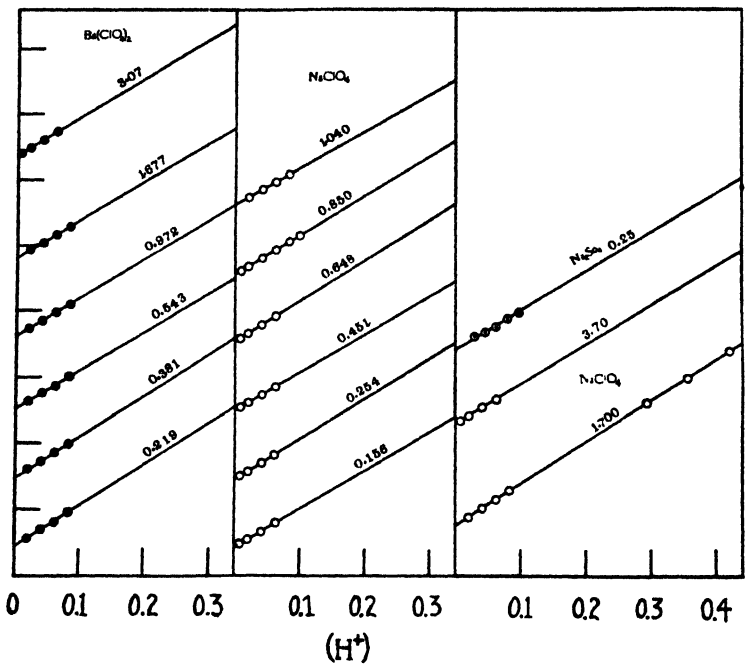

FIG. 1. ABSENCE OF SALT EFFECT ON REACTION 4

Since the curves have been shifted vertically to prevent superposition, numerical values for the ordinates have not been given. For every curve, any value of k' may be found from table 1 if the ionic strength, given above the curve, is used to identify the curve in question.

ent of it.[2] (We shall not at present be concerned with the curvature apparent in figure 2 at the highest ionic strengths.) Granting the plausible kinetic interpretation that has been advanced for the rate law, equation 2, we must conclude that, although reaction 3 shows a "linear" salt effect

[2] Two factors insure that the salt effect on k_1^0 will not appreciably alter the slopes of the lines in figure 1: at low (H^+) the change in μ_c caused by adding acid is so small that k_1^0 is not sensibly affected; at high (H^+) the contribution of reaction 3 to the absolute rate is relatively small; in the region of intermediate (H^+), both effects are operative.

TABLE 1

Detailed experimental results for figure 1

Sodium iodide–perchloric acid solutions. Temperature, 25°C. Initially $(H_2O_2) = 8 \times 10^{-4}$ moles per liter. Average $(I^-) = 5.72 \times 10^{-2}$ moles per liter. Values of (H^+) are averages.

SERIES	ADDED SALT	CONCENTRATION OF ADDED SALT	μ_c^*	(H^+)	k'
		moles per liter		*moles per liter*	
2	$Ba(ClO_4)_2$	0 054	0 219	0.02022	0.0563
				0.04130	0.0706
				0.0623	0.0811
				0.0834	0.0964
3	$Ba(ClO_4)_2$	0.108	0.381	0.02030	0.0617
				0 04130	0.0715
				0.0624	0 0860
				0.0834	0.0990
4	$Ba(ClO_4)_2$	0 162	0 543	0.02021	0 0640
				0.04130	0.0773
				0.0623	0.0872
				0.0834	0.1010
5	$Ba(ClO_4)_2$	0 305	0.972	0 02030	0 0730
				0.04130	0.0850
				0.0623	0.098
				0.0834	0.110
6	$Ba(ClO_4)_2$	0 540	1 677	0.02023	0.0936
				0 04130	0.1040
				0.0624	0.1170
				0.0834	0.1290
7	$Ba(ClO_4)_2$	1.004	3.07	0.00760	0.1400
				0.02020	0.1490
				0.04130	0.1610
				0.0624	0.1740
8	$NaClO_4$	0.0985	0.156	0.00763	0.0480
				0.02027	0.0550
				0.04128	0.0670
				0.0624	0.0794
9	$NaClO_4$	0.0197	0.254	0.00767	0.0510
				0.02021	0.0575
				0.04130	0.0698
				0.0623	0.0820
10	$NaClO_4$	0.394	0.451	0.00761	0.0530
				0.02024	0.0600
				0.04130	0.0730
				0.0623	0.0850

TABLE 1—*Concluded*

SERIES	ADDED SALT	CONCENTRATION OF ADDED SALT	μ_c*	(H^+)	k'
		moles per liter		*moles per liter*	
11	$NaClO_4$	0.591	0.648	0.00764	0.0580
				0.02026	0.0660
				0.04123	0.0790
				0.0623	0.0920
12	$NaClO_4$	0 793	0.850	0.00758	0.0600
				0.02025	0.0680
				0 04126	0.0800
				0.0623	0 0940
				0 0832	0.1070
				0.0998	0.115
13	$NaClO_4$	0 983	1.040	0 02024	0.0730
				0 04129	0 0850
				0 0623	0 0961
				0 0832	0.1085
14	$NaClO_4$	1.643	1 700	0 02030	0.0880
				0 04130	0.1024
				0.0623	0 1152
				0 0834	0.1277
				0.2934	0 2600
				0.3571	0 2990
				0 4202	0 3400
15	$NaClO_4$	3 643	3 70	0 00753	0.1330
				0.02024	0 1410
				0.04130	0 1540
				0.0623	0.1670
16	Na_2SO_4†	0.0644	0.25	0 03048	0.0619
				0.04520	0.0684
				0.0621	0.0775
				0.0800	0 0890
				0 0987	0 0984

* μ_c represents the ionic strength, in concentration units, due to iodide and added salts; its value for each series is given above the curve in figure 1 corresponding thereto.

† Formation of HSO_4^- has been considered in calculating (H^+); the uncertainty of this correction precluded measurements in more concentrated sodium sulfate solutions.

of reasonable magnitude, reaction 4 is altogether without the exponential salt effect predicted by the Brönsted theory (2). Before these conclusions are discussed, we shall consider briefly the results of a group of experiments

designed to reveal whether reaction 4 has appreciable salt effect at low ionic strengths.

In these experiments the iodine formed could be accurately titrated with thiosulfate before any marked concentration change occurred, so that the

TABLE 2

Summary of experimental results in figures 1 and 2, and table 1

SERIES	μ_c*	k_1^0	k_1
	$Ba(ClO_4)_2$ as added salt		
1†	0 0572	0 69	10 4
2	0.219	0 77	10 8
3	0 381	0 84	10 7
4	0.543	0 91	10 2
5	0.972	1 08	10 2
6	1 677	1 40	10 3
7	3 07	2 41	10 2
	$NaClO_4$ as added salt		
8	0 156	0 75	10 7
9	0.254	0 78	10.5
10	0 451	0.85	10.2
11	0 648	0 93	10 8
12	0 850	1 00	10 3
13	1 040	1 07	10 0
14	1 700	1 33	10 8
15	3 70	2 26	10 5
	Na_2SO_4 as added salt		
16	0 25	0 74	10.4
Arithmetic mean of k_1 values. ..			. 10.4 ± 0.06‡

* μ_c represents the ionic strength, in concentration units, due to iodide and added salt.

† These values were obtained without added salt (see reference 7) and are not plotted in figure 1.

‡ The average error of the mean has been computed from a "least squares" formula; this procedure seems applicable, for the value of k_1 for each series was determined independently of the other data—i.e., no attempt was made to select "best" values of k_1 after all the data were at hand.

"method of constant rates" (1, 8) could be employed. To the reaction mixture, at room temperature and containing starch as indicator, thiosulfate solution was added from a buret at the minimum rate that would prevent the appearance of the starch blue, while the flask containing the

mixture was kept in constant motion.[3] The thiosulfate consumed in a minute measures the rate at which iodide is oxidized in reaction 1; from this rate, $k'/(I^-)$ may be calculated. Values thereof obtained at different values of (H^+) have been plotted against (H^+) in figure 3; in table 3 the results are summarized.

The results in table 3 demonstrate that this experimental method is capable of less accuracy than the "analytical method" (7) employed to obtain the data in table 1; further, since reaction 4 is responsible, on the average,

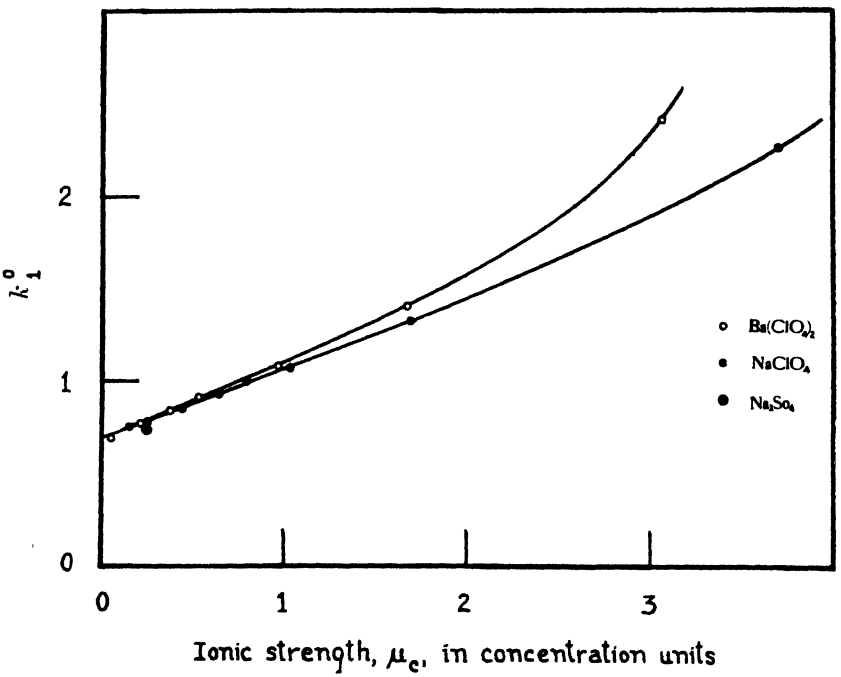

FIG. 2. SALT EFFECT ON REACTION 3
(Cf. table 2)

for only one-tenth of the absolute rate, experimental errors will appear greatly magnified in k_1. We believe, however, that the large number of experiments tends to compensate these inaccuracies; and since the results

[3] Gradual addition of the thiosulfate so that no great excess of it is ever present seems preferable to initial addition of the whole amount, for its oxidation by the hydrogen peroxide is thus greatly reduced. (Cf. Abel: Monatsh. **28**, 1239 (1907).) This oxidation is accelerated somewhat by hydrogen ion; the difference between the k_1 values of table 2, and 10.4, the value from table 1, may conceivably be due to some reaction like this.

Our experimental method is a modification of that first used by Harcourt and Esson (Phil. Trans. Roy. Soc. **157**, 117 (1867)).

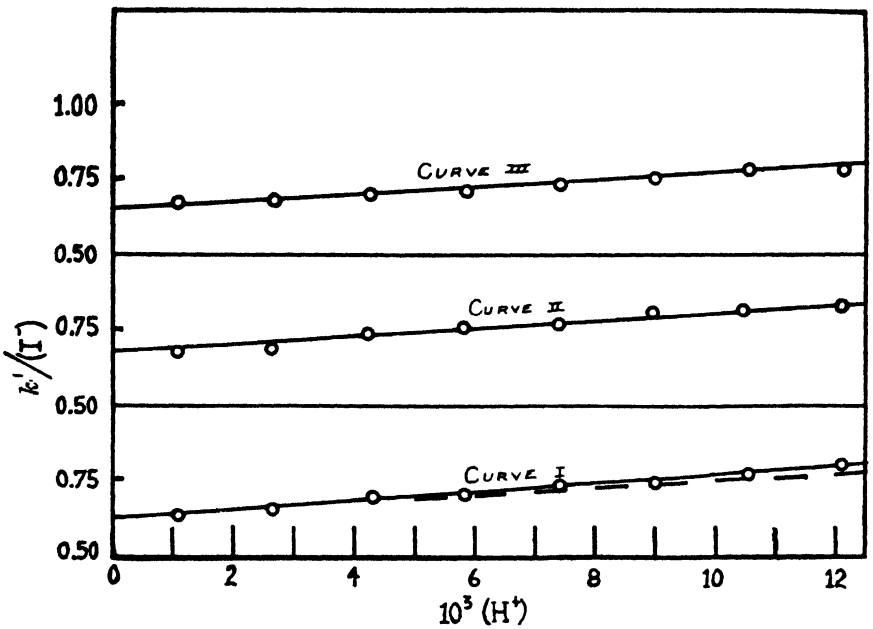

FIG. 3. ADDITIONAL SALT EFFECT MEASUREMENTS

Cf. table 3. The radius of the circles corresponds to a change in $(k'/(I^-))$ of 0 02.

TABLE 3

Data for experiments of figure 3

$(H_2O_2) = 1.23 \times 10^{-2}$ moles per liter; (H^+) variable

SERIES NO.	$(I^-) \times 10^3$	$(NaClO_4)$	k_1^0 (23°)	k_1 (23°)	k_1^0 (25°)	k_1 (25°)
I	1.06	0.00	0.63	11.7	0.74	13.2*
II	1.05	0.113	0.68	12.3	0.79	13.8
III	1.06	0.568	0.65	11.7	0.76	13.2

Corresponding table 1 values: k_1^0 = 0.69(I), 0.75(II), and 0.89(III); k_1 = 10.4 (all three series).

*0.005 is an average value for the ionic strength of Curve I, figure 3. The dotted line below this curve has been drawn through $k'/(I^-)$ values, each corrected for the positive salt effect on k_1^0. Only for the point at highest acid is this correction, which was determined in additional experiments, appreciably larger than the experimental error; the dotted line gives k_1 = 12, which is *lower* than the values at higher ionic strengths. (Did the Brönsted theory apply, it should be *higher*.) We have given the uncorrected value in table 1 because the correction is itself uncertain. Since μ_c does not change greatly along Curves II and III, a similar correction need not be applied.

are self-consistent, we do not hesitate to offer them as confirmatory evidence for the conclusion that reaction 4 is without salt effect. Emphasis should be placed, not on the difference between 13 (the approximate table 3 value of k_1) and 10.4 (the accurate table 1 value), but on the fact that the table 3 values agree with each other. Although the experimental error is rather large ($\pm$ 10 per cent seems a fair estimate), it is probably not over one-fourth the change in γ^2 over the range of ionic strengths covered in table 3. We must conclude, therefore, that the experiments of figure 3, covering ionic strengths from $\mu_c = 0.005$ (see footnote to table 3) to $\mu_c = 0.5$, furnish no evidence for the exponential salt effect predicted by the Brönsted theory.

DISCUSSION OF RESULTS

In discussing the experimental results we shall employ a terminology differing slightly from what is usual.[4]

An inspection of figure 2 makes evident that, below $\mu_c = 2$, k_1^0 may be considered a linear function of the ionic strength. As is well known, such an effect may be interpreted as an equilibrium salt effect if the *intimate mechanism*

$$\text{Rapid equilibrium: } H_2O_2 + I^- \rightleftarrows H_2O_2 \cdot I^- \tag{3a}$$
$$\text{Rate-determining: } H_2O_2 \cdot I^- \rightarrow H_2O + IO^- \tag{3b}$$

is assumed for reaction 3: the concentration of $H_2O_2 \cdot I^-$ could vary linearly with the ionic strength, for I^- and this complex each carry a single negative charge and therefore have similar activity coefficients. (Thus, for series 5, table 1, $(H_2O_2 \cdot I^-)$ would be $\frac{1.08}{0.69}$ times as large as for series 1.) The curvature, which becomes pronounced as μ_c increases above 2, might well be due to a superimposed medium effect, more marked with barium perchlorate; this superimposed effect might be responsible also for the steeper

[4] By the general term "salt effect" we understand the effect, to a first approximation similar for all electrolytes, on the rate of a reaction of changing the ionic strength. (Skrabal (Z. physik. Chem. **3B**, 247 (1929)) prefers the more accurate term "electrolyte effect," which he has been using for many years.) Three kinds of salt effects may now be recognized: *equilibrium salt effects*, caused by the shift in an equilibrium, which accompanies a change in ionic strength and alters the concentration of a substance involved in a rate-determining step; *kinetic salt effects* to which no definite cause can be assigned, but with which the various attempts to introduce activity coefficients into rate laws (the activity theories of reaction rate) are principally concerned; and *medium effects*, which result when electrolyte addition has been so large that the reaction now proceeds in what is virtually a new solvent. There seems to be no sharp line of demarcation between medium effects and pronounced kinetic salt effects.

Our "equilibrium" salt effect is identical with the "secondary kinetic" salt effect of Brönsted (2), while we have omitted "primary" in naming his "primary kinetic" salt effect.

slope of the barium perchlorate line in figure 2. The results in this figure do not differ markedly from some obtained by Harned and his collaborators (3, 4, 5, 6) by a different experimental method.

When we come to consider reaction 4, one thing is immediately obvious; the experimental results cannot be interpreted by the use of any activity theory of reaction rates, for k_1 is independent of the ionic strength, and the introduction of thermodynamic activity coefficients into the rate law would therefore destroy the constancy experimentally observed. The discovery of additional cases of this kind would furnish strong evidence for the belief that no theory leading to rate laws that involve thermodynamic activity coefficients can hope to prove generally valid.

From another point of view, also, this absence of salt effect, so unexpected in the light of past experience, is disturbing. It has been shown (7) that

$$k_1^0 = 4.91(10^9)e^{\frac{-13,400}{RT}}, \text{ from 0 to 50°C} \tag{5}$$

and

$$k_1 = 4.58(10^8)e^{\frac{-10,450}{RT}}, \text{ from 0 to 40°C.} \tag{6}$$

Reactions 3 and 4 thus possess nearly identical heats of activation and nearly identical Arrhenius constants; this confirms the expectation, based on the fact that a single hydrogen ion represents the only difference apparent between these two rate-determining steps, that their intimate mechanisms will be very similar. In this event, however, we would have two closely related reactions, of which one (reaction 3) exhibits a normal salt effect, while the other shows none—a state of affairs not at all reasonable. In particular, if reaction 4 is to have an intimate mechanism

$$\text{Rapid equilibrium:} \quad H_2O_2 + I^- \rightleftharpoons H_2O_2 \cdot I^- \qquad \text{(4a) also (3a)}$$

$$\text{Rate-determining:} \quad H_2O_2 \cdot I^- + H^+ \rightarrow H_2O + HIO \qquad \text{(4b)}$$

patterned after equations 3a and 3b, we would have to make the unwelcome assumption that the linear positive salt effect (which, together with the low Arrhenius constant, 4.91 (10^9), supports equations 3a and 3b) found for reaction 3 is somehow miraculously compensated in reaction 4b. (Thus, if reaction 4b in the above scheme takes place, it—like reaction 3b—should be influenced by the $\frac{1.08}{0.69}$-fold increase in ($H_2O_2 \cdot I^-$) for series 5, table 1, over that for series 1.) Of course, equations 4a and 4b do not exhaust the possibilities; the statistically complex process we recognize as reaction 4 may be formulated differently, but we have found no formulation that can explain the absence of any appreciable salt effect for the reaction.

If results like ours are not restricted as to the type of reaction for which they occur, it would seem advisable to treat salt effects, with the exception of those involving known equilibria, from a more empirical point of view than is at present customary.

CONCLUSION

The salt effect on the rate at which hydrogen peroxide is reduced in acid solution by iodide ion has been studied over a large range of ionic strengths, sodium and barium perchlorates serving as added salts. Of two rate-determining steps proceeding simultaneously and independently, the one (a second-order reaction involving hydrogen peroxide and iodide ion) exhibits the linear type of salt effect to be normally expected, while the other (a third-order reaction involving hydrogen peroxide, and hydrogen and iodide ions) is without any appreciable salt effect whatever. This behavior contradicts the bulk of past experience and is irreconcilable with any activity theory of reaction rates; it suggests that salt effects in general might perhaps be profitably treated from a point of view more empirical than that now customary. An alternative terminology for the discussion of salt effects has been proposed.

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PHYSICOCHEMICAL STUDIES ON GUM ARABIC SOLUTIONS

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I. ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF ARABIC ACID AND ITS SALTS

There are several reasons why gum arabic serves as an especially satisfactory colloid for use in experiments of the nature to be described in the following papers. It forms definitely colloidal solutions in water. It is easily prepared from the commercially obtainable sorts in the manner described below and the various preparations, using commercial gum from the same source, i.e., Sudan gum, have been found, in the experience of the author, to be identical in their properties. The gum can be electrodialyzed until it is practically free of ash, forming a fairly strong acid, the equivalent weight of which does not vary appreciably from sample to sample. This indicates that all salt-forming groups (acid groups) in the colloidal micella are available to react within a very short period of time with the added alkali (in contrast to silicic acid solution, for example). The arabic acid is stable against hydrolysis by its own hydrogen ions (agar, for instance, is partially hydrolyzed upon electrodialysis). The acid and all of its salts are soluble in water in all proportions, an advantage over soap solutions where many salts and the free acids are generally insoluble in water. Solutions of the arabic acid or its salts are relatively stable against attack by microörganisms, no change in the solutions being detectable after standing at room temperature without preservative for days. And finally, it has no isoelectric point, i.e., is not amphoteric. It acts always as an acidic substance. The acid group in the gum arabic is probably a carboxyl group. The electrodialyzed gum contains no sulfur or phosphorus.

The purified gum is prepared by dissolving the sorts in water to form a 5 to 10 per cent solution which is filtered, and enough hydrochloric acid then added to make the solution about 0.1 N acid. Alcohol is then added until the gum is precipitated as a white granular mass, which is separated from the mother liquor by filtration. The gum is redissolved and reprecipitated twice, and then partially dried *in vacuo* to remove most of the

alcohol. It is then dissolved in a small amount of water and electrodialyzed in a three-compartment cell with frequent changes of water in the electrode compartments until no further change in conductivity of the gum solution is observed. Cellophane membranes are used. The electrodialysis requires about a week to go to completion, during which time the current is maintained below 0.3 ampere in order to prevent too much heat from being developed in the solution. Toward the last, the current drops off to a very small value, owing to the absence of electrolytes in the electrode compartments. Considerable calcium hydroxide appears in the cathode chamber during the early stages of electrodialysis. The final solution of the gum is strongly acid (approximate pH = 2.0), and its ash content has dropped to about 0.05 per cent of the dry weight of the gum. Its titration curve is that of a fairly strong acid. One gram of the acid requires 85×10^{-5} equivalents of base to neutralize it, indicating its equivalent weight to be 1175. This value is identical with that obtained by Thomas and Murray (5) upon a sample of gum similarly prepared.

The various salts of arabic acid used in the following experiments were prepared by neutralizing the acid with the hydroxides of the metals the salts of which were desired, and drying the solutions *in vacuo* at 70°C., after which the salts were kept dry until used. The acid itself was not prepared in the dry form, but its concentration in a stock solution was determined and this solution used wherever experiments on the free acid were made.

Specific conductivity measurements were made upon the arabic acid and its salts at 25°C., using a conductivity cell of the Washburn type, the cell constant being 0.3560. The usual Wheatstone bridge arrangement was used with earphone detector and an alternating current of 1000 cycles. The solutions were made up on the weight basis, the concentrations being shown in the tables as the number of grams of dry colloid per 1000 grams of water. Triple distilled water was used as solvent, this having a specific conductivity value of 2 to 4×10^{-6} mhos.

The specific conductivities of the solutions, as given in the tables, have been corrected for the conductivity of the water and, upon the assumption that conductance through the volume occupied by the micellae would be negligible, the specific conductivities of the solutions are corrected for the volume occupied by the colloid in the solution. Where μ is the fraction of the total volume of the solution which is occupied by the gum, the observed electrical resistance in the conductivity cell must be multiplied by the factor, $1 - \mu$, in order to find the resistance offered by the intermicellar liquid, i.e., the true resistance of the solution. The value, μ, may be calculated according to the equation

$$\mu = 1 - \frac{1000s}{(1000 + a)H}$$

where s = the specific gravity of the solution at 25°C., H = that of water at 25°C., and a = the number of grams of the colloid dissolved in 1000 g. of water. This correction is of the order of 6.4 per cent in the most concentrated solution used (i.e., 100 g. of colloid in 1000 g. of water) and rapidly decreases in magnitude as dilution increases.

The equivalent volumes of the solutions are calculated as the number of cubic centimeters of solution containing one equivalent of the colloid electrolyte, according to the equation

$$V = \frac{1000 + a}{85 \times 10^{-5} \times s \times a}$$

In order to obtain the equivalent volume of the solution after correction for the volume occupied by the colloidal micellae (as appears in the tables), the value V must be multiplied by the above factor, $1 - \mu$, i.e.,

$$V_e = V \times (1 - \mu)$$

The equivalent conductivities, $\Lambda = V_e \times \kappa$, for the acid and for five salts, viz., potassium, sodium, lithium, calcium, and strychnine salts of the acid, are given in tables 1 and 2 and are plotted in figure 1 against the log of V_e, the equivalent volume. The acid shows a maximum at very high dilution, while the salts of the alkali and alkaline earth metals show curves similar to those found by McBain and his students (3) for the salts of the high molecular weight fatty acids, i.e., soaps. With all these salts of arabic acid a minimal equivalent conductivity is found at a concentration of about 0.0025 equivalent per liter (log V_e = 5.6). Besides this similarity of form between the equivalent conductivity–concentration curves of arabic salts and the soaps, there are several marked dissimilarities which should be pointed out. The minimum occurs with soap solutions at an equivalent concentration of 0.1 as compared with 0.0025 for the acacia salts. Also the equivalent conductivities of soaps are unexpectedly high, being between two and three times the mobility value of the cation alone, while with the acacia salts the equivalent conductivities of the salts of the alkali metals are only of the order of the mobilities of the corresponding cations. In the case of the calcium salt it is much lower than that of calcium ion (if complete dissociation of the salt were to be assumed).

From the data obtained on the alkali metal and calcium salts alone, it is possible to offer various possible explanations for the form of curve shown. Although the arabic acid acts as a fairly strong acid and the alkali metal salts of even weak acids are nearly completely ionized at the equivalent concentrations studied in these experiments, we could assume something less than 100 per cent ionization and could then apply the explanation offered by McBain for the data obtained from the soap solutions. That is, the increase in conductivity for concentrations lower than that at

TABLE 1

Conductivity data on arabic acid at varying dilutions

a	s	V_e	κ corrected $\times 10^5$	Λ_{acid}	pH	$[H^+] \times 10^5$	V_{H^+}	Λ_{H^+}	$[T]$	$[HA] = [T] - [H^+] \times 10^5$	$\frac{[A^-]}{[HA]}$	$-\log\frac{[A^-]}{[HA]}$	$pK = pH - \log\frac{[A^-]}{[HA]}$	α
grams		*cc.* $\times 10^{-3}$					*cc.* $\times 10^{-3}$		*equiv.* $\times 10^5$					
100	1 030	11.80	260.4	30 71	2.082	828.0	120.75	315.0	7961	7133	0.1161	0.935	3.017	0.1041
80	1.024	14 76	231.6	34.18	2.125	750.0	133.33	309.0	6450	5700	0.1316	0.881	3 006	0.1163
60	1.018	19.70	196.2	38.62	2.195	638.0	156.80	307.5	4895	4257	0.1499	0.824	3.019	0.1303
50	1.015	23.61	175.1	41.35	2.245	568.5	176.00	308 0	4106	3537	0.1608	0.794	3.039	0.1385
40	1.012	29 51	151.0	44 58	2.304	496.2	201 60	304.8	3307	2811	0.1765	0.753	3.057	0.1501
25	1.0075	47.22	108.2	51 05	2.441	362 0	276.30	299 0	2090	1728	0.2094	0.679	3.120	0.1732
20	1.006	59 00	89.8	53.00	2.520	302 0	331 10	297.5	1677	1375	0.2197	0 658	3.178	0.1802
10	1.003	118.10	52.55	62.07	2.751	177.4	563 80	296 2	843.5	666.1	0.2760	0 575	3.326	0.2102
5.0	1.0015	236.10	29.35	69.30	2 995	101.2	989.00	290.5	423 5	322.3	0.3139	0.503	3.498	0.2391
2.5	1.000	472.00	16.07	75 80	3 255	55.55	1800.0	289.5	212.0	156.5	0.3550	0.450	3.705	0.2620
1.25	0.998	944.00	8.66	81.75	3.531	29.43	3400.0	294.5	106.0	76.57	0.3845	0.415	3.946	0.2778
0.625	0.997	1891.50	4.59	86.80	3 805	15 66	6390.0	293 2	52.87	37.21	0.4210	0 376	4.181	0.2962
0.3125	0.997	3788.0	2 35	89 00	4 108	7.80	12825.0	301.2	26.40	18.60	0.4190	0.378	4.486	0.2955
0.1563	0.997	7570.0	1 15	87.10	4.416	3.84	26050 0	299 5	13.21	9.37	0.4095	0.387	4.803	0.2906
0.0714	0.997	16560.0	0 43	71 20	4 867	1.36	73600 0	316 0	6 04	4.68	0.2905	0.537	5.404	0.2251
H_2O	0.997		0.21											

a = grams of colloid dissolved in 1000 g. of water.
s = specific gravity of the colloid-containing solution.
V_e = equivalent volume of the solution.
κ = specific conductivity of solution at 25°C.
Λ = equivalent conductivity of solution.
V_{H^+} and Λ_{H^+} = equivalent volume and equivalent conductivity on basis of hydrogen-ion concentration.
$[H^+]$, $[A^-]$, etc. = concentration per liter of solution.
pK = negative logarithm of the dissociation constant.
α = degree of ionization of the colloid electrolyte.

TABLE 2

Conductivity data on neutral salts of arabic acid at varying dilutions

a	s	V_e	LOG V_e	POTASSIUM ARABATE		SODIUM ARABATE		LITHIUM ARABATE		CALCIUM ARABATE		STRYCHNINE ARABATE	
				$\kappa \times 10^5$	Λ	$\kappa \times 10^5$	Λ	$\kappa \times 10^5$	Λ	$\kappa \times 10^5$	Λ	$\kappa \times 10^5$	Λ
		cc. $\times 10^{-3}$											
50	1.0165	23 60	4.373	250 00	59 00	182 50	43.10	149 20	35 25	106.10	25.05	78 80	18.60
40	1.0135	29.55	4.470					121 80	36 00				
30	1.0100	39.35	4.595							61 00	24.00	48.40	19.05
25	1.0084	47.20	4 674	123 70	58 35	91.80	43.30						
20	1 0067	59.10	4 772					60 95	36.05	38.75	22 90	33.10	19.56
10	1 0033	118.10	5.072	46.40	54 80	35.14	41 50	29 83	35.25	18.00	21.27	17.28	20.40
5	1 0016	236.00	5 373	22.25	52.55	17.06	40.35	14 69	34 70	8 55	20.20	8.97	21.17
2.5	1.0000	472.00	5 674	10.98	51 82	8.50	40.12	7 26	34.30	4.35	20.55	4.74	22.38
1.25	0.998	944.50	5.976	5.54	52.30	4.36	41.20	3 76	35.50	2.25	21.25	2 55	24.10
0.625	0.997	1891.50	6.277	2.88	54.45	2.28	43.12	2 02	38.20	1.22	23.07	1.35	25.55
0.3125	0.997	3788.10	6.578	1 51	57.20	1 24	46.95	1.09	41 30	0.70	26 50	0.79	29.90
0.156	0.997	7570 00	6 879	0.82	62.10	0.67	50 70						
H_2O	0.997			0.35		0 40		0 23		0.24			

which the minimum is observed would arise from a continuous increase in degree of ionization with increased dilution, while the increase in conduc-

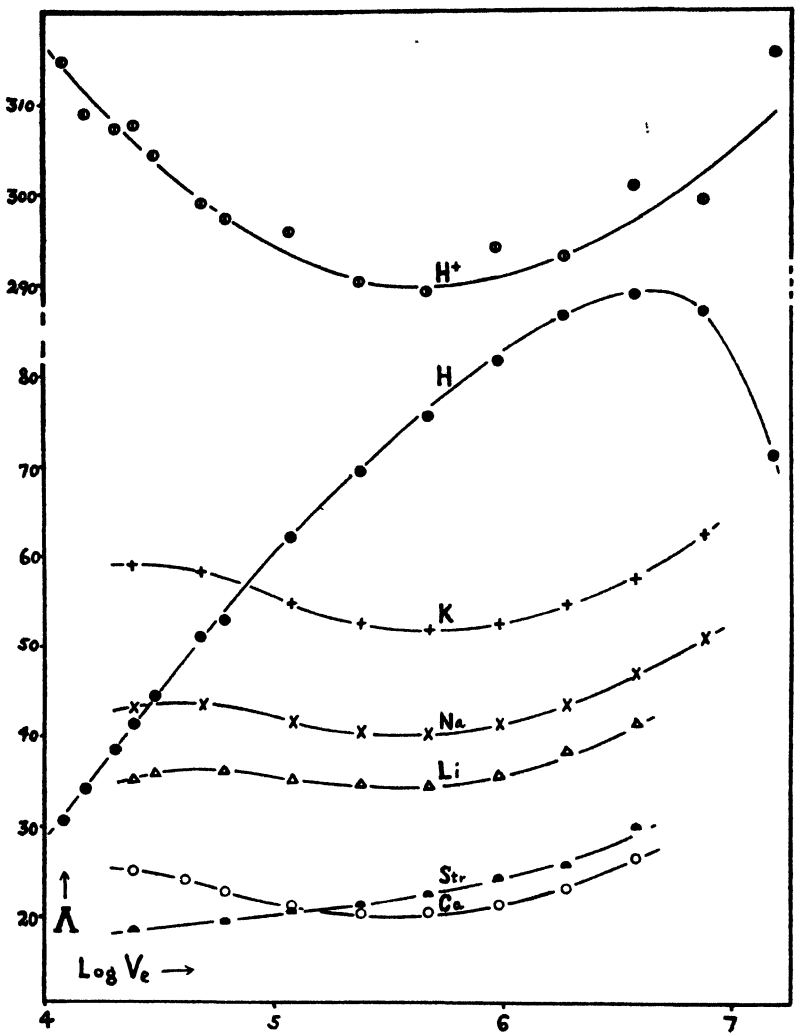

FIG. 1. CURVES SHOWING THE VARIATION OF THE EQUIVALENT CONDUCTIVITY (Λ) OF SOLUTIONS OF ARABIC ACID AND ITS VARIOUS SALTS, WITH CHANGE IN EQUIVALENT VOLUME (V_e)

Curve marked (H^+) shows the equivalent conductivity on the basis of the ionized fraction of the acids, while curve marked (H) shows the equivalent conductivity on the basis of total acid present in solutions.

tivity for concentrations higher than that at which the minimum is found would result from an increase in the degree of aggregation of the colloidal anion accompanied by a marked increase in the charge density on the sur-

face of the micella (decrease in surface area per unit charge). A correspondingly higher migration velocity of the micella would result, this accounting for the increased transference of electric current.

Again, assuming less than complete ionization of the alkali metal salts of arabic acid and explaining the increase in Λ with increased dilution as above, it is possible that the increase in Λ with increased concentration results not because of increased agglomeration of the anionic carrier but because of an increase in the percentage of total current carried by surface conducting ions. Surface conductance measurements on glass and cellulose surfaces indicate that the ions present in the region of the interface can move more freely through the surface region under the influence of an electric field than they can through the bulk of the solution. If, in the present case, owing to greater concentration of the colloid, the number of contacts between micellae increased to a large degree, it is possible that a marked increase in the current carried by the solution might result when surface conductance took place at the instant of contact between the micellae. That agglomeration would follow such contacts between the micellae does not necessarily follow, because these hydrophilic colloids do not depend upon their electric charge to maintain their stability.

A third explanation of these data, and one which seems to fit the additional data obtained upon the acid and its strychnine salt, arises from conclusions drawn by Lewis (2) concerning the validity of Kohlrausch's assumption of constant ion mobility with change in concentration of the electrolyte. Lewis, from an analysis of existing data, showed that the transference number of an ion (i.e., the fraction of total current carried by that ion) may change radically with change in electrolyte concentration of the solution, and therefore the relative mobility of the ions must be changing with concentration. This change becomes most noticeable when the differences in mobility of the two ions involved are markedly unequal. Kohlrausch's assumption of constant ion mobility is therefore not strictly true, and it is possible that the mobility of an ion may vary with the concentration. Lewis found a minimum to exist in the transference number–concentration curve for several ions in true solution. If the large fraction of the current carried by an electrolyte is carried by one ion, the transference number of the other ion being very low, it is to be expected that the changes in mobility of the ion of higher transference number would be noticeably reflected by similar changes in the Λ-concentration curve of the electrolyte. Since, too, the relative change in mobilities with concentration of the two ions is more marked the greater the difference in the absolute mobilities of the ions, it is to be expected that as the relative mobilities of the ions became nearer 1 (i.e., as the absolute mobilities became more nearly equal), the Λ–concentration curve would no longer show evidences of those influences at work in the solution.

The mobility of the arabate ion is not known, but its transference num-

ber must be very low, as evidenced by the fact that the equivalent conductivities of the lithium, sodium, and potassium salts are somewhat lower than the values to be expected from the cation alone if the salt were 100 per cent ionized. That these salts are nearly totally ionized is indicated by the fact that the equivalent conductivity of the hydrogen ions, in the experiments with the acid, shows a change with concentration similar to that of the salts. The curve for the equivalent conductivity of the acid on the basis of hydrogen-ion concentration, lies below the usually accepted mobility value of hydrogen ion (i.e., 315), a distance which is relatively equal to the distance that the curves from the salts lie below the mobility value of their respective cations. The curve marked H^+ in figure 1 is that plotted from values of Λ_{H^+} for the acid calculated on the basis of hydrogen-ion concentrations at the various dilutions. The hydrogen-ion concentrations were determined electrometrically upon the same solutions that were used for the conductivity experiments. It is seen from the curve that current carried by equal amounts of ionized acid is at a minimum in the same region of concentration (of total colloid) as that in which a minimum is observed in the equivalent conductivities of the salts. If we can assume that electrometric measurements of hydrogen-ion concentration with a hydrogen electrode give a correct measure of the hydrogen-ion activity in the solution, we have here definite proof that the cation mobility is changing with concentration of the colloid electrolyte. In this case the greater part of the current must be carried by the hydrogen ions. If the same is true of the lithium, potassium, and sodium salts it is evident that these must be ionized to a very great extent. The same cannot be said of the calcium salt. Here the degree of ionization must be of the order of 50 per cent.

It can be assumed then that the mobility of the arabate ion is low. Since the effect of concentration upon mobility of the cation associated with the arabate ion should, according to this theory, become less apparent as the mobilities of the cations approached that of the arabate ion, it is proper that we should observe that the Λ–concentration curve tends to flatten out (i.e., the minimum becomes less pronounced), as the mobility of the cation decreases. The curve for the H^+ salt shows a very deep cusp on the curve, while that of the lithium salt is nearly flat, though still showing a distinct minimum. With the, presumably, slow moving organic cation, strychnine, the cation mobility has reached a sufficiently low value so that there no longer exists a minimum in the Λ–concentration curve for its salt with arabic acid, that is, there is not sufficient difference between the mobilities of the arabate and strychnine ions to cause variation in the mobilities of the cation to such a degree as to become apparent in the Λ–concentration curve for this salt.

This theory does not rule out the possibility of a reversible agglomeration

of the micellae taking place as the concentration increases. It does, however, postulate that the variation in the Λ–conductivity curves is largely due to variation in the absolute mobility of the cations which, in the case of this particular colloid electrolyte, appear to act as conductors for almost all of the current which passes through the solution. The maximum in the Λ–concentration curve for the acid coincides closely with a maximum in percentage ionization as indicated from hydrogen-ion measurements. An explanation of this observation will be given in the succeeding section in terms of the existence of a reversible polymerization or peptization occurring with change in concentration of the acid in solution.

II. THE DISSOCIATION "CONSTANT" OF ARABIC ACID

When an electrodialyzed gum arabic solution is titrated with an alkali and the course of the hydrogen-ion concentration in the solution followed electrometrically with a bubbling hydrogen electrode, the titration curve so obtained is found to be that of a fairly strong acid. The curve is smooth like that of any monobasic acid, although the molecular (or micellar) weight of the arabic acid must be many times its equivalent weight. The neutralization equivalent of the acid does not change with dilution and is equal to 85×10^{-5} equivalents per gram of the acid. The time required for equilibrium to be attained after addition of an increment of alkali is only of the order of time needed for complete mixing of the solutions. It would appear, therefore, that the acid (replaceable) hydrogens of the colloid exist at the surface of the micellae and are readily available to react with the added alkali. Certainly no part of the colloid exists in the form of the acid anhydride, which requires hydrolysis to take place before reaction with the alkali can occur. (As is the case with a silica gel micella, where the inner portion of the micella consists of SiO_2 which must hydrolyse to H_2SiO_3 before reaction with sodium hydroxide to form the sodium silicate.) Thomas and Murray (5) showed that no further alkali was bound beyond a pH of 7, i.e., all acid hydrogens of the acid react with the alkali before pH = 7 is reached.

Since the acid, which obviously cannot be a monobasic acid, shows a titration curve essentially that of a monobasic acid, it is necessary to picture the acid hydrogens of the acid as being so far apart in the molecule that the ionization of one group has practically no intramolecular influence upon the tendency of the other groups to ionize, or else that every ionizable hydrogen present has a dissociation constant somewhat different from every other one and that these dissociation constants for the various acid groups are rather uniformly distributed throughout the buffer range of the acid. In the first case, the calculation of the dissociation constant of the acid as a monobasic acid would be allowed. In the second case such a calculation would mean nothing, except that the constant so obtained

would refer to an average dissociation tendency of all the acid groups present in the acid.

The dissociation "constant" of arabic acid has been calculated, in this paper, upon the assumption that the acid acts as a monobasic acid, from dilution data on the acid and from the titration curves at various dilutions.

TABLE 3

Titration data for arabic acid at two concentrations

NaOH PER GRAM	pH	$[H^+]$ $\times 10^6$	$[T]$ $\times 10^6$	$[Na^+]$ $\times 10^6$	$[A^-] = [Na^+] + [H^+]$ $\times 10^6$	$[HA] = [T] - [A^-]$ $\times 10^6$	RATIO $[A]/[HA]$	LOG RATIO	pK
50 g. acid per 1000 g. water									
equiv. $\times 10^6$									
0	2.24	575 0	4250	0	575	3675	0.1565	−0.805	3 05
7.08	2.45	355.0	4250	354	709	3541	0 2001	−0 699	3 15
14.17	2.64	230.0	4250	708	938	3312	0.2831	−0.548	3 19
21.25	2 81	155.0	4250	1062	1217	3033	0.4010	−0.397	3 21
28.33	3.00	100 0	4250	1417	1517	2733	0 5550	−0 256	3.26
35.41	3 15	70.8	4250	1771	1842	2408	0.7550	−0 116	3.27
42.50	3.34	45.8	4250	2125	2171	2079	1 045	+0.019	3 32
49 58	3 50	31 6	4250	2480	2512	1738	1.445	+0.160	3.34
56.66	3 68	20.9	4250	2833	2854	1396	2 042	+0.310	3 37
63.73	3 90	12.6	4250	3187	3200	1050	3 048	+0.484	3 42
70 82	4 13	7 41	4250	3541	3548	702	5.055	+0.704	3 43
77.91	4 60	2 50	4250	3895	3898	352	11.070	+1 045	3 55
85 00	7 00		4250	4250	4250				
0.625 g. acid per 1000 g. water									
0	3.82	15.12	53.1	0	15.1	38.0	0.398	−0 401	4 22
14 17	4.11	7.77	53.1	8.85	16 6	36.5	0 455	−0 342	4.45
28.33	4 43	3.72	53.1	17 71	21.4	31 7	0 675	−0.170	4 60
42.50	4 95	1.12	53.1	26 60	27.7	25.4	1 091	+0.038	4.91
56.66	5.39	0 408	53.1	35.40	35.8	17.3	2 070	+0.316	5 07
70.82	6.01	0 098	53.1	44 30	44.4	8 7	5 110	+0 708	5.30
85.00	7.00		53.1	53.10	53.1				

These calculations are given, with the data from which the values were calculated, in tables 1 and 3 and are shown graphically in figures 2 and 3.

The values obtained for the acid at various dilutions were calculated from measurements on the same solutions as those used for conductivity measurements, where the hydrogen-ion concentrations were determined electrometrically. The pK (i.e., the negative logarithm of the dissociation constant) was calculated according to the equation

$$pK = pH - \log \frac{[A^-]}{[HA]}$$

the value of $[A^-]$ being taken as equal to the measured $[H^+]$, and $[HA]$ being taken as equal to the total equivalent concentration of the acid $[T]$

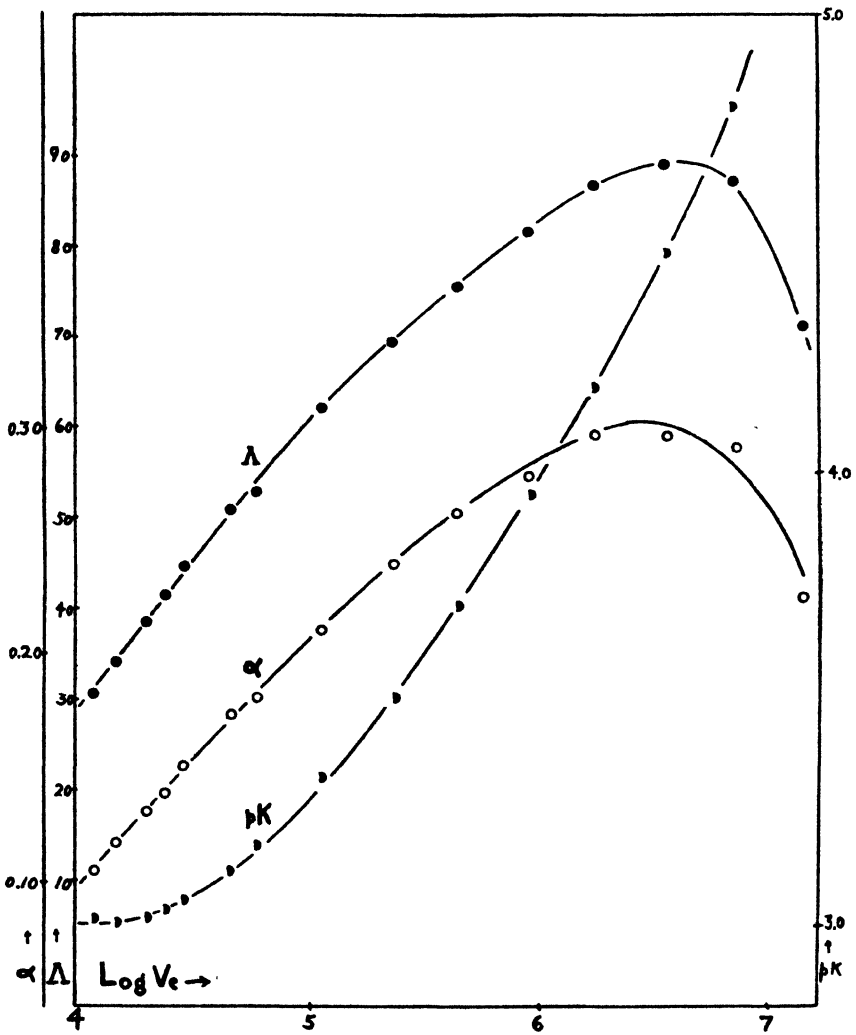

FIG. 2. CURVES SHOWING THE MANNER IN WHICH THE EQUIVALENT CONDUCTIVITY (Λ), THE DEGREE OF IONIZATION (α), AND THE DISSOCIATION "CONSTANT" (K) OF THE ACID (PLOTTED AS THE NEGATIVE LOGARITHM OF K) VARY WITH THE CONCENTRATION OF THE SOLUTIONS OF THE ACID (PLOTTED AS THE LOGARITHM OF THE EQUIVALENT VOLUME (V_e))

minus $[H^+]$. The degree of ionization of the acid at the various dilutions is also calculated as

$$\alpha = \frac{[H^+]}{[T]}$$

In figure 2 it is seen that α reaches a maximum at about the same concentration of the acid at which the equivalent conductance, Λ, of the acid reaches a maximum. Also it is seen that the pK value of the acid at con-

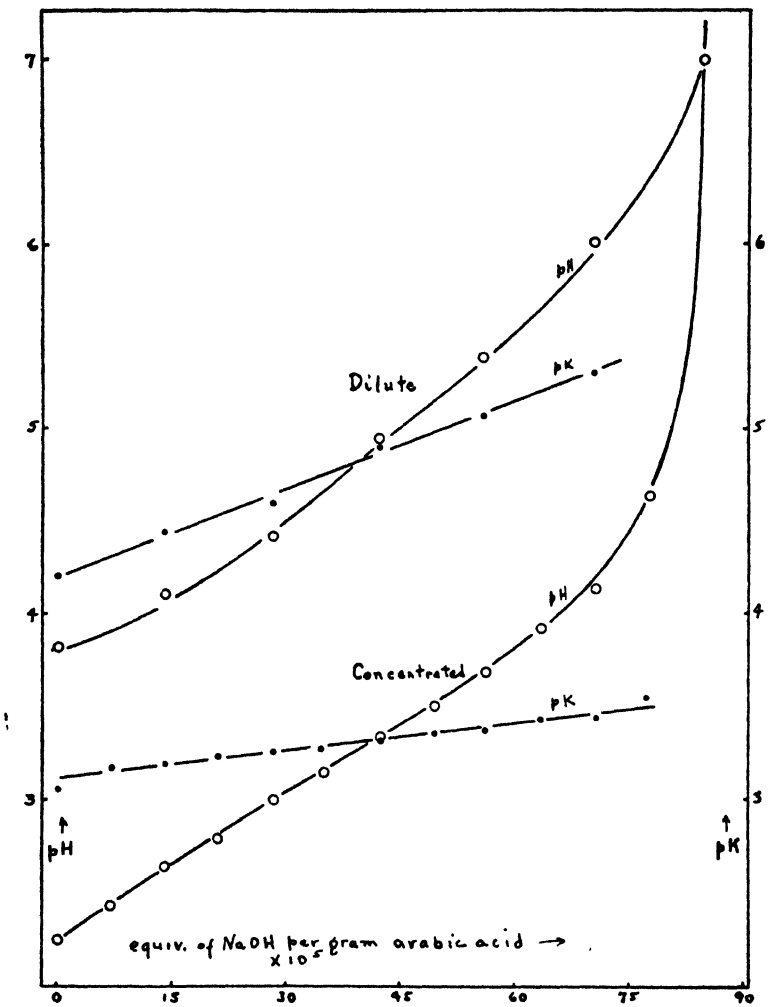

FIG. 3. TITRATION CURVES OF ARABIC ACID AT THE TWO CONCENTRATIONS, 50 G. AND 0.625 G., RESPECTIVELY, OF THE ACID IN 1000 G. OF WATER, AND THE VARIATION IN THE CALCULATED VALUES OF THE DISSOCIATION "CONSTANT" (K) OF THE ACID (PLOTTED AS pK) WITH THE DEGREE OF NEUTRALIZATION

centrations higher than 50 to 60 g. per 1000 g. of water (equivalent concentration of 4 to 5 $\times$ 10^{-2}) becomes fairly constant in the neighborhood of 3 ($K = 1 \times 10^{-3}$), but with increased dilution the value of pK increases

continuously. This must mean that the acid is acting more and more like a very weak acid as the dilution increases. This conclusion is substantiated by the fact that the degree of ionization of the acid reaches a maximum and rapidly falls off with increased dilution. The observed α curve is the resultant of two tendencies: the one, the increased ionization with dilution, i.e., that commonly observed with solutions of all but the very strong acids; the other, the decrease in the dissociation constant of the acid with increased dilution, i.e., its tendency to dissociate decreases as it acts more and more as a very weak acid. The first factor predominates at the higher concentrations, and not until the rate of change in pK is very high (i.e., at highest dilution) does this factor predominate in the determination of the course of the α curve.

From the titration curves, the value of pK was calculated in a manner similar to that given above. Here, however, the sodium salt formed was considered to be completely ionized and $[A^-]$ was taken to equal $[H^+] + [Na^+]$, where $[H^+]$ was measured electrometrically and $[Na^+]$ was calculated from the amount of sodium hydroxide added. [HA] then would equal $[T] - [A^-]$. Figure 3 shows the titration curve and calculated pK values for the acid at two concentrations, one at a concentration of 50 mg. of acid per 1000 g. of water and the other at a concentration of 0.625 g. of acid per 1000 g. of water. These measurements were made upon solutions prepared by adding the desired amount of sodium hydroxide to solutions containing equal amounts of acid and then diluting the resulting solutions to contain equal weights of water. Thus there was no change in weight of solvent throughout the titration curve shown, and the varying pK calculated cannot be due to the dilution factor shown to exist in the above experiment with the acid.

Both of these titration curves show the acid to be completely neutralized at pH = 7. In both cases the calculated pK increases as neutrality is approached. At the higher concentration this drift in pK is not so great as at the lower concentration. And, in accordance with the dilution data on the acid, the value of pK increases with dilution. This shift of the pK value with neutralization may be taken to indicate that the latter of the above-mentioned pictures of the dissociation tendencies of the acid groups is more nearly the correct one. As alkali is added to the acid, the acid groups showing the greater dissociation tendency are first neutralized, and the average dissociation "constant" of the remaining acid groups is of a lower order of magnitude than before this fraction of the acid hydrogen was replaced by alkali cations.

Two conclusions to be drawn from these data on the apparent dissociation constant of the acid are: first, the various acid groups present have dissociation constants which are distributed in a continuous manner over the buffer range of the acid in such a way as to give a titration curve which

resembles that of a monobasic acid in that there is only one definite buffer range; and second, the average dissociation constant for all these groups decreases at a continuously increasing rate with dilution.

This latter conclusion may be taken to indicate a readily reversible change in the size of the micella accompanied by a shift in the tendency toward ionization of the acid groups on the micella.

An analogous situation is found in the case of silicon dioxide sols. Rabinowitch and Laskin (4), from measurements of the electrical conductivity and potentiometric titration curves for an electrodialyzed solution, found a value of the dissociation constant of colloidal silicon dioxide equal to $K_1 = 2 \cdot 10^{-4}$. Their titration curves showed the solution to have a buffer region at pH 3 to 5. Willstätter and coworkers (6) prepared silicic acid solutions by hydrolysis of silicon tetrachloride in water in presence of silver oxide and obtained an acid which, immediately after preparation, showed a freezing point depression which indicated it to be molecularly dispersed. They found that polymerization immediately set in and proceeded at a more or less rapid rate thereafter, finally resulting in a colloidal solution of polysilicic acid of uncertain composition. They made potentiometric titration curves on their freshly prepared acid and upon the same after several days. They found a buffer region for the fresh solution at about a pH of 6.5, which shifted to lower pH as polymerization proceeded. The calculated value of the dissociation constant for their freshly prepared acid (i.e., pK is taken to equal the pH of half-neutralization in the buffer region of the acid) is found to be $K_1 = 5 \times 10^{-7}$.

Hogg (1) determined the value for the dissociation constant of true dissolved silicic acid from the degree of hydrolysis of sodium silicate solutions and found $K_1 = 10^{-9}$ and $K_2 = 10^{-13}$.

All this work seems to indicate that the greater the degree of polymerization of the silicic acid, the greater becomes the value of the dissociation constant and the strength of the acid. If we can assume a reversible polymerization of the arabic acid with increasing concentration, it is possible that the shift in the average dissociation constant of the acid may result from this in a manner similar to that observed with silicic acid solutions. One marked difference between these two colloids is that polymerization of the silicic acid solution is accompanied by dehydration of a part of the acid, while there is no indication that the number of readily reacting acid groups in the arabic acid changes with concentration (or, presumably, dispersion and polymerization).

SUMMARY

1. Equivalent conductivity values for arabic acid show a maximum at a concentration of approximately 0.00025 equivalent per liter. A maximum in the degree of ionization occurs at the same concentration.

Equivalent conductivity values for the potassium, sodium, lithium, and

calcium salts and for the ionized acid (i.e., calculated on basis of hydrogen-ion determinations) all show a minimum at a concentration of 0.0025 equivalent per liter. The prominence of this minimum varies to a degree which is roughly proportional to the ordinarily used mobility values of the cations employed, and totally disappears from the equivalent conductivity–equivalent volume curve for the strychnine salt of the acid.

It is postulated that the observed variation in the Λ–concentration curves is due to a change in the absolute mobility of the cations with concentration (the anion mobility being comparatively low) in accordance with the conclusions of Lewis concerning the variability with concentration of the transfer number for ions in ordinary electrolyte solutions, which also state that the effect is more marked when the mobilities of the two ions of the salt are markedly different.

It is to be concluded that the ionic activities of the cations present in these colloid electrolyte solutions will be different if measured electrometrically (as with the hydrogen-ion electrode) and if measured conductimetrically (assuming constant mobility of the ions), the degree of difference varying with concentration.

2. The titration curve for arabic acid shows only one buffer range. However it does not act as a monobasic acid, but as one the acid groups of which have varying ionization constants which are rather uniformly distributed throughout the buffer range of the acid. Calculated dissociation constants of the acid (regarding it as monobasic) give the average dissociation constant of all the acid groups present in the acid.

At any given concentration of the acid the dissociation "constant" decreases with the percentage neutralization, indicating that those groups of high dissociation constant are the first neutralized by added base and that this leaves the average dissociation constant of the remaining (unneutralized) groups at a lower value.

The dissociation "constant" of the acid decreases rapidly with increased dilution from a value of about $K = 1 \times 10^{-3}$ for a concentration of 50 to 100 g. of the acid per 1000 g. of water to near $K = 2 \times 10^{-7}$ at infinite dilution (extrapolation value). It is assumed that reversible peptization of the micella occurs when the solution is diluted and that this is accompanied by a marked decrease in the dissociation tendency of the acid groups present on the micella. Only in concentrated solutions does the acid act as fairly strong acid, though in all cases except, perhaps, in extremely dilute solutions the acid is completely neutralized at a pH of 7.

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THE OPTICAL ACTIVITY OF CAMPHOR IN ALCOHOLIC SOLUTIONS

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During the course of an investigation of the different methods used for the determination of camphor in spirits of camphor, it was necessary to prepare a large number of alcoholic solutions of camphor. These solutions were read in the polariscope and the specific rotations were calculated. Camphor is one of a number of organic substances which give different values for specific rotation when different strengths of alcohol are used as solvents. The rotation varies also for different amounts of camphor in the same percentage strength of alcohol.

One may find a number of references in the literature which give the specific rotations of camphor in ethyl alcohol. Among these may be mentioned Landolt (3), Moreau (5), Kazay (2), Malosse (4), Peacock (7), Francois and Luce (1), and Owen (6). However, no comprehensive study in which both factors (percentage camphor and strength of alcohol) are varied has been reported for the complete series of alcoholic solutions of camphor.

The samples of camphor used were the purest refined products which could be obtained on the market. The camphor was resublimed at least once; the first ten per cent coming over as sublimate was discarded, as was the last ten per cent remaining in the distilling flask. Pure ethyl alcohol which had been distilled over quicklime was used to make up the various dilutions of alcohol.

The camphor solutions varied in strength from 1 per cent to the highest concentration which the particular strength of alcohol used would dissolve. All solutions were made with the greatest accuracy and at the uniform temperature of 20°C. The solutions in each case were weight to volume solutions. Ten readings for each of the solutions were made in the polariscope at 20°C. The specific rotation was calculated by use of the formula

$$\text{Specific rotation} = \frac{\frac{a}{2.8835} \times 100}{l \times c}$$

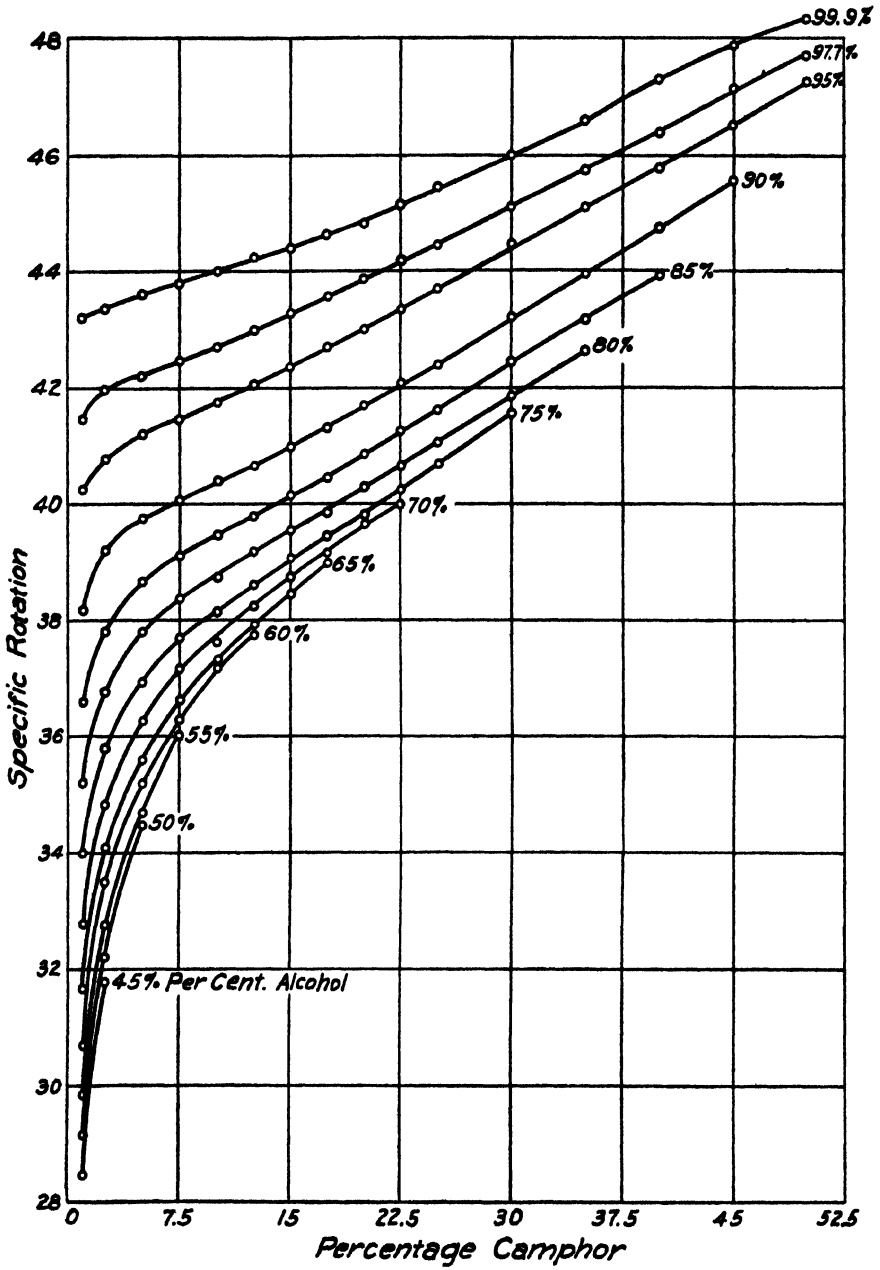

FIG. 1. CURVES SHOWING CHANGES IN SPECIFIC ROTATION FOR VARIOUS AMOUNTS OF CAMPHOR DISSOLVED IN DIFFERENT STRENGTHS OF ALCOHOL

where a is the polariscope reading, l is the length of the tube in decimeters and c is the concentration in grams per 100 cc. of solution.

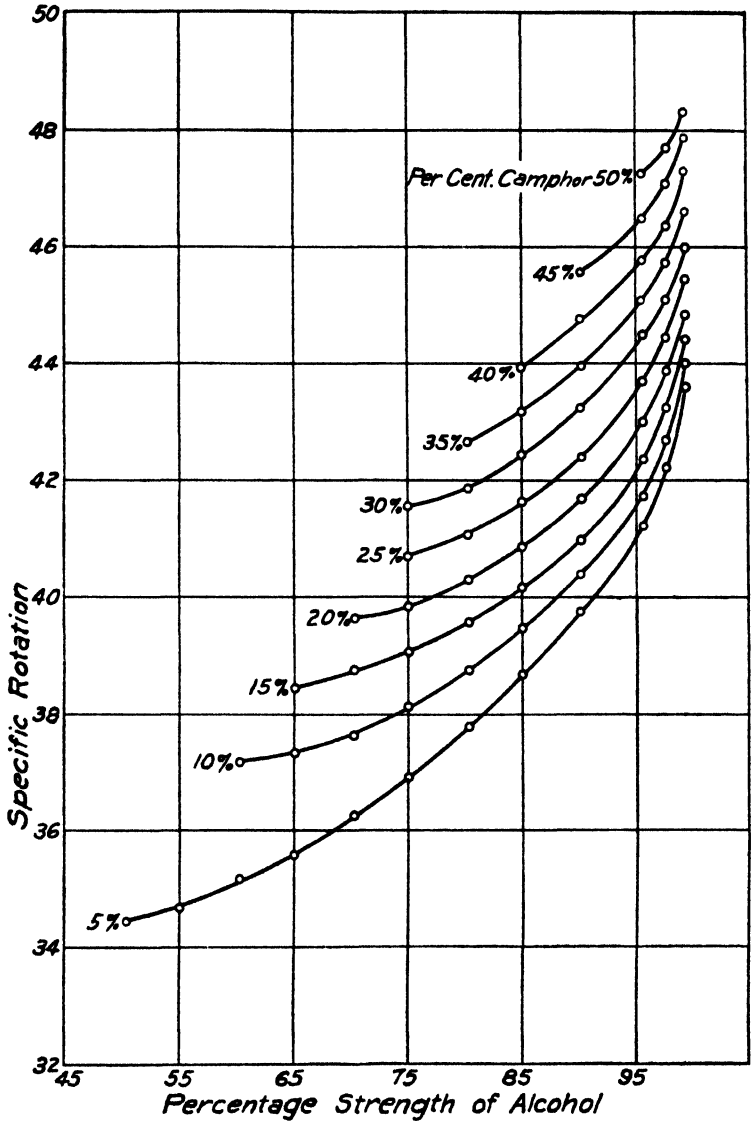

FIG. 2. CURVES SHOWING CHANGES IN SPECIFIC ROTATION FOR VARIOUS AMOUNTS OF CAMPHOR DISSOLVED IN DIFFERENT STRENGTHS OF ALCOHOL

The results are shown graphically in figures 1, 2, and 3. Figure 1 shows the curves obtained when the specific rotation is plotted against the percentage camphor. Figures 2 and 3 give the curves obtained when specific

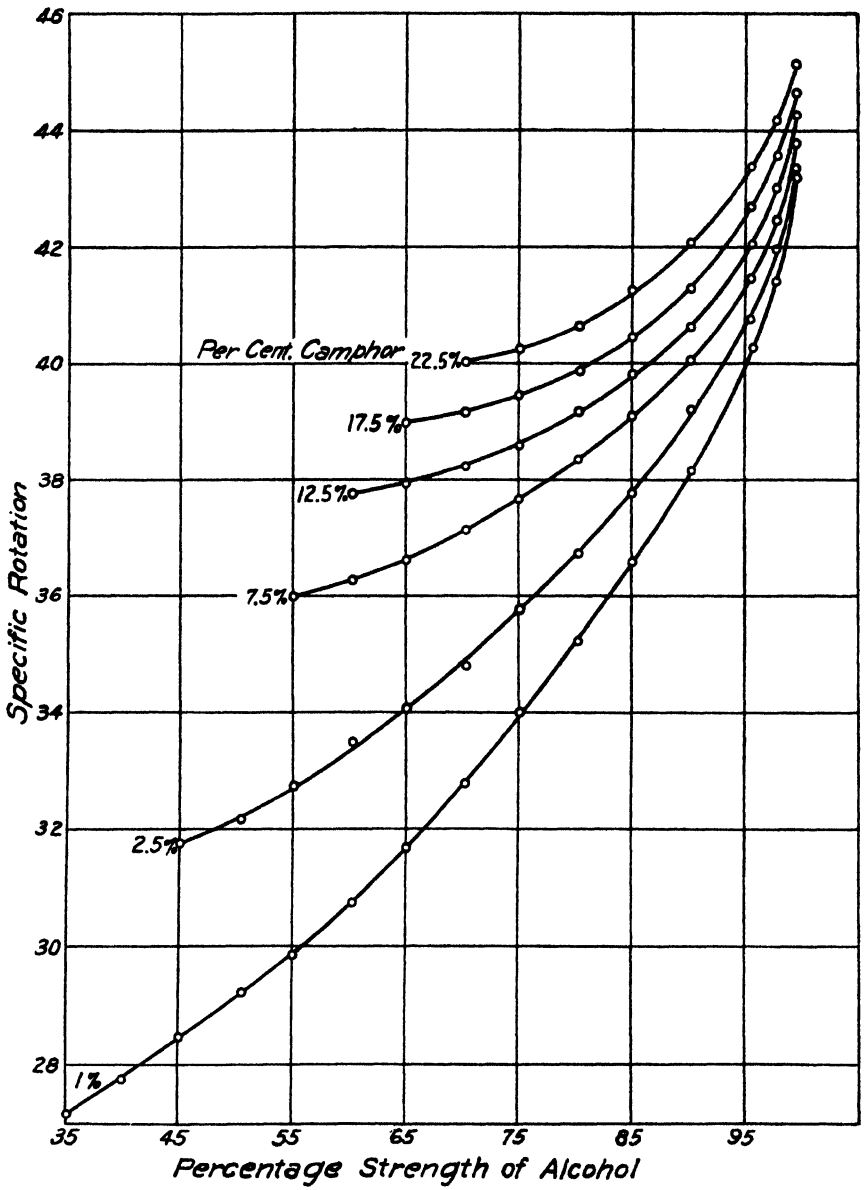

FIG. 3. CURVES SHOWING CHANGES IN SPECIFIC ROTATION FOR VARIOUS AMOUNTS OF CAMPHOR DISSOLVED IN DIFFERENT STRENGTHS OF ALCOHOL

rotation and percentage strength of alcohol are the variable factors. The curves given in these figures offer a practical means of determining an unknown factor when two of the three values—specific rotation, amount of camphor, strength of alcohol—are known.

From the figures we may see that the specific rotation varies considerably with a change in the strength of alcohol or with a change in the percentage of camphor dissolved. The values increase as the strength of alcohol increases. The specific rotation when the camphor content is 1 per cent varies from 27.14 for 35 per cent alcohol up to 43.18 for absolute alcohol. In the same strength alcohol the specific rotation increases as the amount of camphor dissolved increases. For instance, in 95 per cent alcohol the specific rotation varies from 40.24 for 1 per cent camphor up to 47.26 for 50 per cent camphor.

SUMMARY

1. The specific rotations for alcoholic solutions of camphor have been determined when the percentages of alcohol and camphor are varied over wide limits.

2. Curves have been constructed for determining a third factor when the values of two factors are known.

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CHEMICAL ACTION IN THE GLOW DISCHARGE. XIII

Chain Reactions in the Oxidation of Hydrogen in the Positive Column

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In a previous article on the oxidation of hydrogen in the glow discharge (4) it was shown that the explosive mixture could not be ignited in the negative glow, although ignition took place with ease in the positive column. The present research was undertaken, therefore, to contrast the reactivity in these two regions of the discharge, in the hope that it might throw some light on the factors determining propagation and on chain reactions in general.

APPARATUS

The discharge tube was a 5-liter Pyrex flask placed in an electric furnace which could be heated to 500°C. The cathode was an aluminum disc 3.2 cm. in diameter located at the bottom of the flask; the disc was encased in glass except for the top surface The anode was an iron rod supported by a winch mounted on the neck of the flask that extended out of the top of the furnace; the position of the anode could be adjusted at will. The anode was 0.5 cm. in diameter and was encased in glass except at the lower end. The pressure in the system was read with a dibutyl phthalate manometer. The gases used were prepared in the manner described previously.

The rate of reaction was determined from the change in pressure per unit time. The rate in the positive column was obtained by subtracting the rate in the negative glow from the over-all rate. Unless otherwise stated all data were taken at room temperature.

RESULTS

The effect of pressure

The effect of pressure on the rate of reaction in a 2-cm. length of positive column is shown in figure 1. The discharge current was 10 ma.

Curve I is the observed rate, curve II the voltage, and curve III the volts required to synthesize one molecule of water. The values given are for

the initial rates. The pressure vs. time curves from which the rates were obtained show the rate to be about constant for the first few minutes of each run, and then to decrease slowly with time.

A comparison of curves I and II shows that the rate increases more rapidly than the voltage, especially at the higher pressures. In consequence the power consumed per water molecule formed is nearly constant at the lower pressures, but decreases appreciably as the pressure is increased.

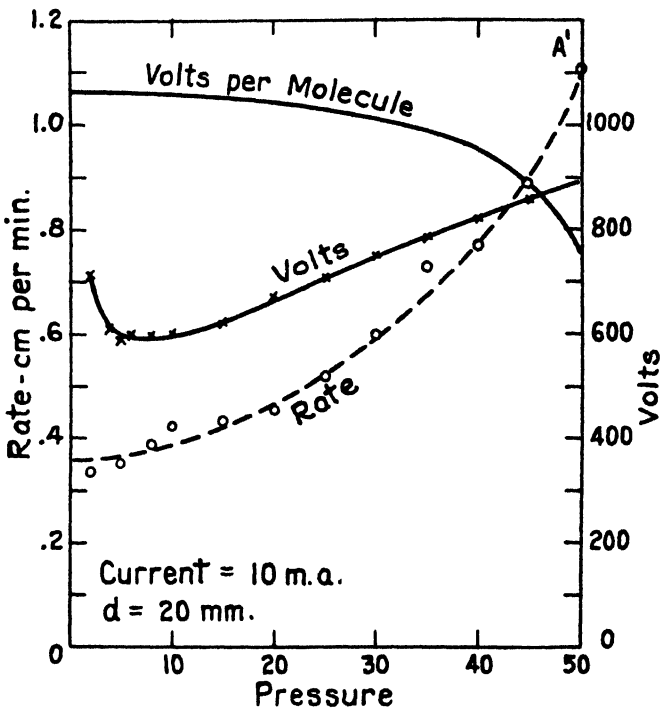

FIG. 1. THE EFFECT OF PRESSURE ON THE REACTION RATE

These results are in distinct contrast with those obtained previously in the negative glow, where the rate was shown to increase only very slightly with the pressure.

The effect of the current

The effect of the current on the rate is shown in figure 2.

The electrode separation was 47 mm. for the positive column and 3 mm. for the negative glow. The potential drop between the electrodes was 650 and 375 volts, respectively.

The data show the rate of reaction in the positive column to be propor-

tional to the current below 25 ma. at the pressures used; above this point the rate increased, and the power expended in terms of volts per molecule dropped rapidly to a very small value.

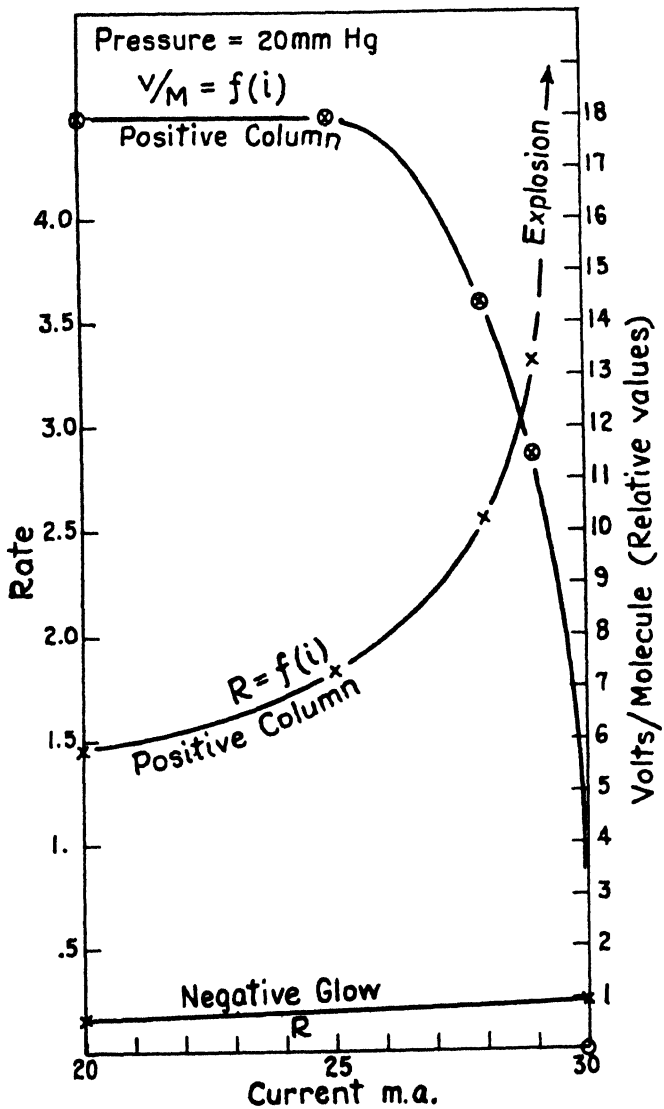

FIG. 2. THE EFFECT OF CURRENT ON THE REACTION RATE

These results are again in contrast with those in the negative glow where the rate was found to be proportional to the current over the range investigated.

The effect of voltage

In the cases where the change in the discharge voltage varied with the current the rate of reaction (R) was proportional to the power input rather than to the current. This is shown in table 1. These results were taken at a pressure of 2.3 cm. of mercury and with an electrode separation of 4.7 cm.

The effect of added gases

The effect of the addition of 3.1 mm. of gas to 18.5 mm. of explosive mixture on the reaction rate is given in table 2. M refers to molecules synthesised, e to electrons, and V to volts. The length of the positive column was 7 mm. and the current was 25 ma. The tests were made with a low

TABLE 1

i	V	R	R/i	$R/iV \times 10^3$
8	490	10 80	1.35	2 76
10	442	11 56	1 16	2.63
12	408	13 00	1 08	2.65
15	372	15 38	1 02	2 75

TABLE 2

The effect of added gases on the reaction rate

ADDED GAS	M/e	V/e	V/M
None	20 2	100	5 0
Hydrogen	20 4	105	5.1
Oxygen	33.4	70	2.1
Nitrogen	21 3	85	4.0
Argon	18 2	70	3.8
Helium	17.3	75	4.9

per cent of added gas in order that the fraction of energy absorbed by this gas should be low.

In the negative glow the rate was proportional to the partial pressure of hydrogen up to 90 per cent added gas, helium had no effect, and nitrogen, oxygen, and argon had a retarding action in the order named.

The effect of various amounts of added gas is shown for argon in figure 3. The difference in the effect of added argon on the reactivity in the two regions of the discharge is very pronounced. In the negative glow argon decreases the rate in a manner very nearly proportional to the amount present. Just the opposite condition exists in the positive column, where the rate increases linearly with the partial pressure of the argon up to 50 per cent added gas.

The effect of water vapor on the reaction rate is shown in figure 4. These curves were obtained from the tangents at different points along the time vs. pressure curves. No correction was made for the change in pressure during the course of the run, since the total pressure used was such that the pressure coefficient was small. The dotted portion of the curve

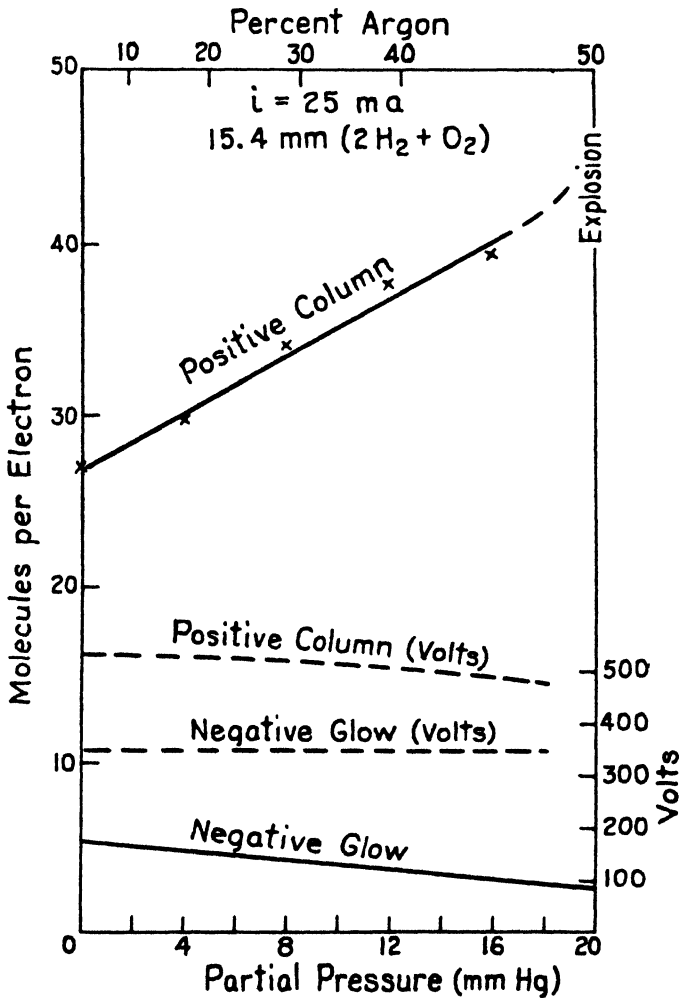

FIG. 3. THE EFFECT OF VARIOUS AMOUNTS OF ARGON ON THE REACTION RATE

represents an extrapolation, made necessary by the fact that the time vs. pressure curves for the currents used showed a small heating effect at the beginning of the run; the extrapolation, therefore, was made from data obtained when the discharge current was 5 ma.

It will be observed that up to 40 per cent water vapor the rate is the

same as in the 2:1 mixture for both the negative glow and the positive column. In this respect its behavior is distinctly different from that of argon. The fact that the rate in the negative glow is unchanged by the addition of water vapor is an indication that water molecules also can fur-

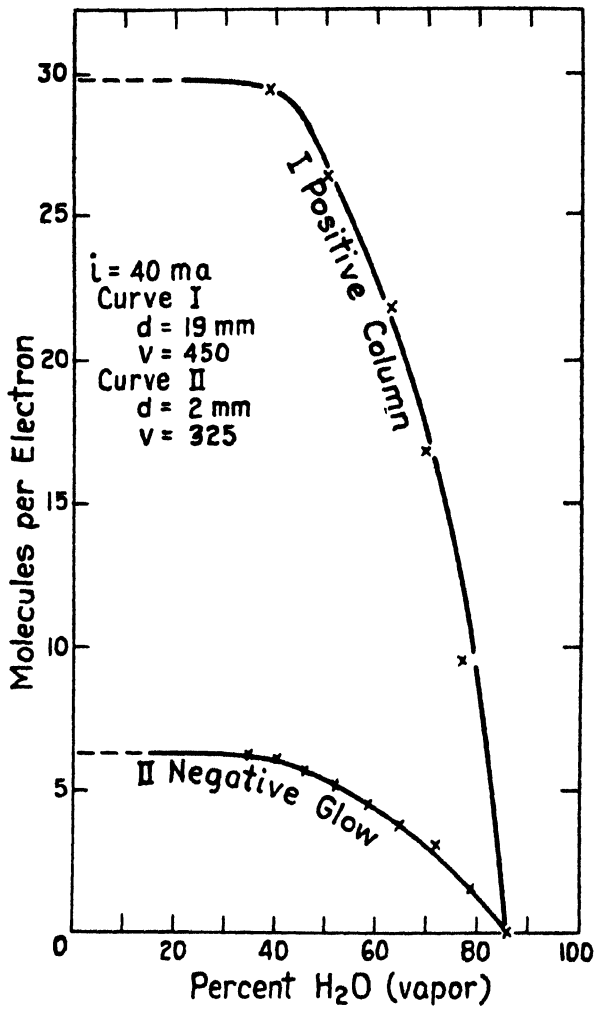

FIG. 4. THE EFFECT OF WATER VAPOR ON THE REACTION RATE

nish reaction nuclei. Substantially the same result has been obtained by Lind and Schiflett using alpha rays (9).

It is interesting to note that the water vapor $-2H_2:O_2$ equilibrium occurs at about 88 per cent water for both regions of the discharge.

The effect of the walls

The effect of the proximity of glass surfaces on the rate was determined by surrounding a discharge between two aluminum rods—3 mm. in diameter, 5 mm. in exposed length, and 2 cm. apart—with glass cases of different sizes. In table 3 are given the results obtained with two such cases. The cylinder was a tube 2.7 cm. long and 3.2 cm. in diameter placed symmetrically over the discharge, the axis of the cylinder being perpendicular to the path of the discharge. The case was 1 cm. on the end, 3.8 cm. on the side, and 2.7 cm. long and was similarly placed.

The values given are for the over-all reaction. M/e is molecules per electron, and V/M is volts per molecule.

The data show that the reactivity probably approaches the same rate for low currents. As the current is increased, the retarding effect exerted by the close proximity of surfaces becomes more and more pronounced. Since both cases were placed to permit unimpaired convection through the

TABLE 3

CURRENT	GLASS CYLINDER		GLASS CASE	
	M/e	V/M	M/e	V/M
20	37.1	13.8	31.5	18.1
25	36.9	13.8	30.5	18.7
30	39.9	12.8	28.0	20.0
35	49.1	10.4	24.7	22.3
38	55.6	9.5		
40	Ignition		22.9	24.0

discharge, the retarding action at the higher currents must be due to limitations in the reaction chains, as is evidenced by the fact that the gas could not be ignited in the rectangular case, while the cylinder had little effect on the ignition energy.

The effect of temperature

In the negative glow the rate of reaction exhibited no temperature coefficient for low current densities and only a detectable positive coefficient for the higher currents. In the positive column the coefficient was more positive, the rate increasing about eightfold for a 300°C. rise in temperature. The effect of temperature is dependent on the conditions existing in the discharge, being influenced by both current and pressure.

DISCUSSION OF RESULTS

A survey of the differences in the reactivity in the negative glow (4) and in the positive column when correlated with the physics of these two

regions may be of some help in understanding the mechanism of reaction involved. In the negative glow evidence was advanced to show that the reaction took place largely about H_2^+ ions and that in comparison O_2^+ ions, atoms, and excited molecules were relatively poor reaction centers. It was shown further that most of the water synthesized reached the walls carrying a positive charge in the negative glow, and as neutral molecules in the positive column.

The difference in the reactivity in the two regions of the discharge is distinct. In the negative glow the M/N ratio is nearly constant, being independent of the pressure and the current density. In the positive column the M/N ratio increases with both the power input and the pressure, due definitely to the presence of reaction chains which are completely absent in the negative glow.

Two alternatives are possible in interpreting the above results. Either some condition is to be found in the positive column that permits the H_2^+ ions to have an M/N ratio far higher than the fixed ratio in the negative glow, or else new active centers come into play that are capable of serving as chain heads.

The physics in the two regions of the discharge differs primarily in the energy of the electrons. In the negative glow measurements of the range of the electrons show that the initial energy corresponds to the entire cathode fall in potential, being of the order of several hundred volts. This energy is dissipated largely in the production of ions (one ion for about 45 volts (5)) and in the excitation of both low and high quantum states. The values of Lehman fix the ratio of $M/H_2^+ = 2$, which is probably more accurate than the value 4 given in the previous communication. A line as well as a band spectrum is emitted. In the positive column, the average energy of the electrons is about 4 or 5 volts, while the maximum energy only slightly exceeds the ionization potential of the gas. The energy is expended largely in the production of ions and in the excitation primarily of lower levels in a large number of molecules. The spectrum ordinarily consists of bands.

It is very improbable that any excited state capable of initiating a chain can be found that exists only in the positive column; ions are abundant in both regions, while atoms and excited molecules, especially those of high energy content, are more prevalent in the negative glow. The expenditure of energy per unit volume of the discharge may be some twenty times greater in the negative glow than in the positive column, as can be seen from figure 4. Roughly the concentration of most excited states will be in proportion to the power expended. In the case of neutral atoms, however, the concentration should be even more pronounced in the negative glow, since they are not produced by direct electron impact but largely, if not entirely, by the dissociation of the excited ions which are present in

appreciable quantities only in the negative glow. The ions formed in the positive column of the direct current low density discharge of the type used are of the normal variety, and hence do not dissociate appreciably.

Since it does not seem possible to find new reactive states existing only in the positive column, one is naturally forced to the other alternative that for some reason chains are set up by the original reaction centers in this region of the discharge, while they are not set up in the negative glow. Chain mechanisms seem limited to three general types: (1) atom chains, (2) excited molecule chains, and (3) cluster chains. A brief consideration of each of these may show the one most capable of explaining the observed facts.

Bonhoeffer and Haber (1) suggest a chain starting with H and continuing consecutively through H and OH. Obviously such a chain should start in the negative glow, where the concentration of H atoms is the highest. The fact that the M/N ratio is constant in this region necessarily eliminates this type of atom chain.

Thompson and Hinshelwood (11) postulate a chain the principal links of which are hydrogen peroxide and activated water molecules. While the mechanism is somewhat indefinite, it is again impossible to see how this type of mechanism could account for the entire reactivity in the discharge without being more pronounced in the negative glow than in the positive column.

In view of what has just been said it does not seem probable that the usual types of chains involving atoms and excited molecules can be used to account for the observed conditions. A modification of the cluster mechanism originally formulated by S. C. Lind offers some prospects of success. The basis of the Lind mechanism, devised for alpha-ray ionization, is that the reaction results from the neutralization of a positive ion or cluster by a negative ion or cluster. Since the postulated reaction does not take place until neutralization occurs, the M/N ratio is limited by the size of the clusters at this instant; obviously, therefore, the ion cannot serve as a chain head. In applying the cluster mechanism to the glow discharge it was necessary to modify the original Lind concept, since neutralization takes place largely at the walls and not in the gas phase as with alpha rays. It was suggested (3), in consequence, that the reaction occurs between just those molecules closely associated about the positive ions, and that the reactivity ceases upon neutralization. The ions, therefore, can serve as reaction centers until neutralized, and hence high M/N ratios or ionic chains are possible. Since the water molecules synthesized in the negative glow reached the walls carrying a positive charge, it is necessary to make the further assumption that reaction does not occur between the molecules associated about the ions until the clusters receive energy from the outside equal to their energies of activation; this may come from colli-

sions with "hot molecules" or from the heat of neutralization by electrons. This type of mechanism will satisfy the demands imposed by the discharge.

The conspicuous difference in the conditions influencing the possible active states in the negative glow and in the positive column appears to be in the length of life of the ions in the gas phase. In the negative glow the ions are driven rapidly to the wall, so that the chance of the ion being struck by an electron or molecule of high energy content is far smaller than in the positive column. The ion, therefore, carries its original cluster to the walls, and the reaction is confined to just those molecules associated about it. In the positive column the life of the ion in the gas phase being longer, its chance of being struck by a body rich in energy is correspondingly large. If this colliding body possesses an amount of energy E sufficient to cause the molecules associated with the ion to react, the total energy of the associate will be $(E + Q)$, where Q is the heat of formation of molecules synthesized. This energy, when Q is large as in the present case, will be sufficient to disrupt the cluster, leaving the ion denuded of its associated molecules; the ion (not necessarily in the original form) is then in a condition to start the process all over. The only difference is that the ion after the disruption of the cluster doubtless contains some fraction ϕ of the energy $(E + Q)$; hence the energy of activation for the new associate will be not E but $E - \phi$. The water thus formed will be liberated in the gas phase largely as neutral molecules.

A typical ionic chain reaction can be illustrated graphically by the following equation:

$$\underbrace{\underbrace{H_2^+ \xrightarrow{H_2 + O_2} [H_4O_2]^+}_{\text{Negative glow}} + E \longrightarrow [H_2O]^+ \longrightarrow H_2O \xrightarrow{H_2 + O_2} [H_4O_3]^+ + E \longrightarrow [H_2O_2]^+ \longrightarrow H_2O}_{\text{Positive column}}$$

Since the water ejected from the cluster contains a large fraction of the energy $(E + Q)$, it can serve as a means of supplying energy E to another cluster.

It should be mentioned that an ionic chain of this type involves no difficulties arising from energy considerations; it is amenable to the general mathematical treatment given by Semenoff (10) for chain reactions; it requires no triple collisions; it accounts for the fact that flame fronts are strongly positively charged, as has been shown in a very ingenious manner by Lewis (6) or as may be seen by placing a flame in an electric field; likewise it accords with the very interesting observations of Lewis and Kreutz, wherein it was shown that flame temperatures are lowered by transverse electric fields (7), and that the ignition temperature of combustible gases is lowered by ionizing the gases previous to their admission to the ignition chamber (8).

On the basis of this mechanism the acceleration in rate of reaction observed in the positive column by oxygen, nitrogen, and argon is easily seen, as these gases, being much heavier than hydrogen, tend to slow down the rate of diffusion to the walls and hence increase the chance of the cluster being struck by an energy-rich molecule. The abnormally large effect of oxygen suggests that O_2^+ ion clusters may also serve as chain initiators provided the energy E of the colliding molecule is sufficiently high. A general extension of this mechanism can now be made to the effect that reaction may occur about any ion or polar molecule capable of associating itself with molecules when this associate is struck by a molecule containing an energy E, equal to or greater than that necessary for activation of the particular associate in question. Since the field of force about an ion or highly polarized molecule is essentially the same as that existing at conducting surfaces, the energy of activation (E) will have the same significance in both cases (2).

The hypothesis just advanced gives for the number of molecules synthesized per unit of current in the negative glow $m = M/N_{H_2^+} \times n$, where n is the number of H_2^+ ions formed, the number of reaction centers being given by $w = n$. This equation also applies in the positive column when propagation is not present; when propagation occurs, another term must be added to take account of the molecules formed in the chain. The probability that the ion will form more molecules than that given by the original M/N ratio depends on the chance of the associate colliding with molecules containing energy equal to $E - \phi$ or greater. Thus the probability of the ion continuing the chain is

$$a = e^{-\frac{E-\phi}{kT}}$$

where k is Boltzmann's constant. The effective number of reaction centers in the positive column, therefore, is given by

$$w = n + wa = \frac{n}{1 - a}$$

If the heat of reaction is small or negative, ϕ will be small compared to E; then a will be small and the wa term will contribute little or nothing to the reaction. This is the case in the negative glow where there is little chance of the new formed water molecules adding their energy to other associates. An increase in Q, combined with the possibility of this energy being returned to a new associate, results in an increase in a with a corresponding contribution by the wa term. Thus when $a = 1$ the chain will be just self-supporting; when $a > 1$ not only will the chain support itself but new reaction centers will be formed in the process, giving rise to branching chains.

Reaction chains of the type just described may be broken in several

different ways. The removal of the clustering centers from the sphere of reaction limits the length of the chain, as may be seen in the negative glow and in the proximity of walls. Lowering the energy density of the gas through which the chain head is moving will cause its reactivity to cease; this is shown by the action of added gases, by the non-proportionality between current and rate, and by the effect of temperature. The selective association of inert molecules about the reaction center may also cause the reactivity to cease. This is illustrated in figure 4 by the shortening of the chains as equilibrium is approached; the chains are broken apparently by the water molecules forming stable clusters with the active centers, thus preventing the association of hydrogen and oxygen.

SUMMARY

1. In contrast to a fixed ratio of $M/H_2^+ = 2$ in the negative glow, the rate in the positive column increases with both current and pressure until the ignition point is reached.

2. The rate of reaction is accelerated by added gases in accordance with their ability to retard diffusion, the effect being almost the opposite to that in the negative glow.

3. The rate is retarded by the presence of walls and accelerated by temperature.

4. The results are interpreted as indicating the presence of reaction chains in the positive column but not in the negative glow.

5. Reasons are advanced to show that the chains must be of the cluster type and cannot consist of atoms or radicals.

6. The mechanism, as well as the factors influencing the cluster type of chains, is discussed.

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THE SOLUBILITY OF AMMONIUM THIOCYANATE IN WATER, METHANOL, AND ETHANOL

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INTRODUCTION

The solubility of ammonium thiocyanate in water at low temperatures has been determined by several investigators (3, 6, 9, 10). No previous determinations of the solubility of ammonium thiocyanate in methanol or in ethanol have been made. These data are of some interest from the standpoint of a study of concentrated solutions—their ideality, non-ideality, and the like.

MATERIALS

The ammonium thiocyanate used was Baker's C.P. grade. The ammonium thiocyanate as received showed a melting point of 149.0°C., but as some solid insoluble materials were present, it was further purified by two recrystallizations from methanol according to Lunge (7), who states that the resulting product is non-hygroscopic. This was found to be the case. The melting point of the ammonium thiocyanate after the above treatment was 149.7°C., which agrees closely with the value 149.6°C. recorded in the literature (5).

It was found necessary to employ all glass or porcelain apparatus in every stage of the process and to avoid possible contact with iron in any form. Solid ammonium thiocyanate or its solution on contact with even an iron spatula gave a pink colored product, no doubt due to the formation of iron thiocyanate, $Fe(SCN)_3$. By using all glass or porcelain apparatus, the resulting recrystallized salt was absolutely white and free from color. It was further observed that when the ammonium thiocyanate was colored with ferric thiocyanate, and the product was heated at 60°C. for a period of hours, the color disappeared.

In addition to the melting point determination, the purity of the ammonium thiocyanate was checked by chemical analysis for its ammonia and thiocyanate content. The ammonia was determined by distillation (2) and showed an average of 22.40 per cent (three determinations) with a maximum deviation of 0.06 per cent. The slightly higher ammonia content than the theoretical may be due to the possible liberation of am-

monia from the thiocyanate group as mentioned by Pfeiffer (8). The thiocyanate content was determined by Volhard's method (15) and showed an average of 76.29 per cent (three determinations) with a maximum deviation of 0.05 per cent.

The water, methanol, and ethanol used in the present research have been described previously (11).

PROCEDURE AND APPARATUS

The synthetic method of Alexejew (1) was employed in making the solubility determinations. The procedure and apparatus used in the present research have been described earlier (11, 12, 14).

Some preliminary data were obtained for the possible conversion of ammonium thiocyanate in water solutions. Samples were heated with water at 100°C. for two hours and then analyzed for ammonium thiocyanate. The ammonium thiocyanate solution when analyzed indicated practically 100 per cent ammonium thiocyanate. This indicated that the procedure had not affected the ammonium thiocyanate. In the determinations that follow the solubility temperatures were considerably lower than 100°C. and were always kept for less than two hours at their respective solubility temperatures. This preliminary data would indicate that no change in the nature of the solute had taken place during the solubility temperature determinations. These findings are in accordance with the results of Waddell (16), who showed that ammonium thiocyanate is very slowly if at all changed at temperatures below 110°C., whether heated alone or in aqueous solution.

It had been pointed out earlier (11) that precautions to insure the presence of small crystals are one of the means of obtaining true equilibrium conditions. An apparent anomaly to this criterion was found in the case of the ammonium thiocyanate–ethanol system. In this system fine crystals could be obtained without difficulty. However, the crystals were so fine as to give a colloidal turbid opalescent solution with the result that, when the ordinary procedure for solubility determinations was followed, the solubility temperatures were overstepped by one or more degrees. To overcome this difficulty, it was found necessary to cool the solution slowly so as to favor the formation of large crystals. Starting with large crystals and thermostating for a period of ten minutes, it was found that the true solubility temperature could be obtained.

EXPERIMENTAL RESULTS

The results of the various ammonium thiocyanate solubility determinations are presented in tables 1, 2, and 3. Concentrations have been calculated and tabulated on both the mol fraction and weight per cent basis. The data were plotted on a large scale according to the method of Hilde-

TABLE 1

Solubility of ammonium thiocyanate in water

(Recrystallized from methanol)

NH_4SCN	SOLVENT	NH_4SCN	NH_4SCN	SOLUBILITY TEMPERATURE
grams	*grams*	*weight per cent*	*mol fraction*	*degrees C.*
1 7853	1 2119	59.57	0.2588	13 00
1 8507	1 1247	62 20	0.2803	18.99
1.6550	0 8933	64 95	0.3043	26 33
1 9970	1.0319	65 93	0.3138	28 82
1.9798	0.8954	68.86	0.3435	36 36
2.3633	1.0105	70.05	0.3567	39.44
2 1629	0 8058	72.86	0.3885	46 92
2 5037	0.8557	74 53	0.4092	51 37
2 8356	0 9465	74.94	0 4154	52.50
2.2651	0 6909	76.63	0 4376	57.23
2 3848	0.6519	78 53	0 4637	62 46
2 2045	0 5451	80.18	0 4890	67 21
2 5536	0 5710	81 73	0 5145	71.53

TABLE 2

Solubility of ammonium thiocyanate in methanol

NH_4SCN	SOLVENT	NH_4SCN	NH_4SCN	SOLUBILITY TEMPERATURE
grams	*grams*	*weight per cent*	*mol fraction*	*degrees C*
0 8746	1 4824	37 11	0 1989	24 58
1.0754	1.6099	40.05	0 2194	32 94
1 3375	1 6549	44 70	0 2538	44 80
0 9994	1 0279	49 30	0 2904	54 76
1 3020	1 0850	54 55	0 3356	64 55

TABLE 3

Solubility of ammonium thiocyanate in ethanol

NH_4SCN	SOLVENT	NH_4SCN	NH_4SCN	SOLUBILITY TEMPERATURE
grams	*grams*	*weight per cent*	*mol fraction*	*degrees C*
0.3867	1.6416	19.07	0 1247	18 45
0.6283	2.2884	21.54	0 1421	33 25
0.6418	2 2545	22 16	0 1469	36 93
0.4571	1.4915	23.46	0 1565	43 36
0.6044	1.6572	26.72	0.1807	57 62
0.5958	1.4855	28 63	0.1953	64 20

brand and Jenks (4), as the log N_2 vs. $1000/T$. The solubilities at rounded temperatures were read off and are given in table 4.

DISCUSSION OF RESULTS

The results of the solubility determinations of ammonium thiocyanate in water were compared with those published by Rudorff (9, 10), Smitts and Kettner (13), Kettner (6), and Foote (3). This comparison is shown in graphic form in figure 1, where the data are plotted according to the method of Hildebrand and Jenks (4). It is felt that the foregoing results are accurate to well within ±0.10°C. of the true solubility temperature.

As shown in figure 1, the curve of the author's data is not a straight line function. If an attempt is made to extrapolate the curve to the point

TABLE 4

Solubility of ammonium thiocyanate in water and alcohols at rounded temperatures

(Expressed in mol fractions of ammonium thiocyanate)

TEMPERATURE	SOLUBILITY OF AMMONIUM THIOCYANATE IN		
	Water	Methanol	Ethanol
degrees C.			
20	0.2831	0.1886	0.1264
25	0.2999	0.1999	0.1322
30	0.3183	0 2119	0 1380
35	0.3381	0.2249	0.1443
40	0.3583	0.2388	0 1512
45	0.3803	0.2545	0.1591
50	0.4031	0 2719	0 1670
55	0.4266	0.2914	0.1757
60	0.4512	0.3136	0.1859
65	0.4764	0 3373	0.1972
70	0 5053	0 3631	0.2095

when the log N = 0, a value below the absolute melting point is obtained, indicating the ammonium thiocyanate does not form an ideal solution in water. Calculations from the vapor pressure data of Foote (3) also indicated that ammonium thiocyanate does not form an ideal solution in water.

The solubility results of ammonium thiocyanate in methanol and ethanol are found in tables 2 and 3. These results are also presented in graphic form in figure 2. It is observed that in the temperature range studied, 20 to 70°C., ammonium thiocyanate in water, methanol, and ethanol does not form straight line functions when plotted as in figure 2. Furthermore, it is seen that ammonium thiocyanate is highly soluble in water, moderately soluble in methanol, and least soluble in ethanol.

When carrying out the solubility determinations of ammonium thiocy-

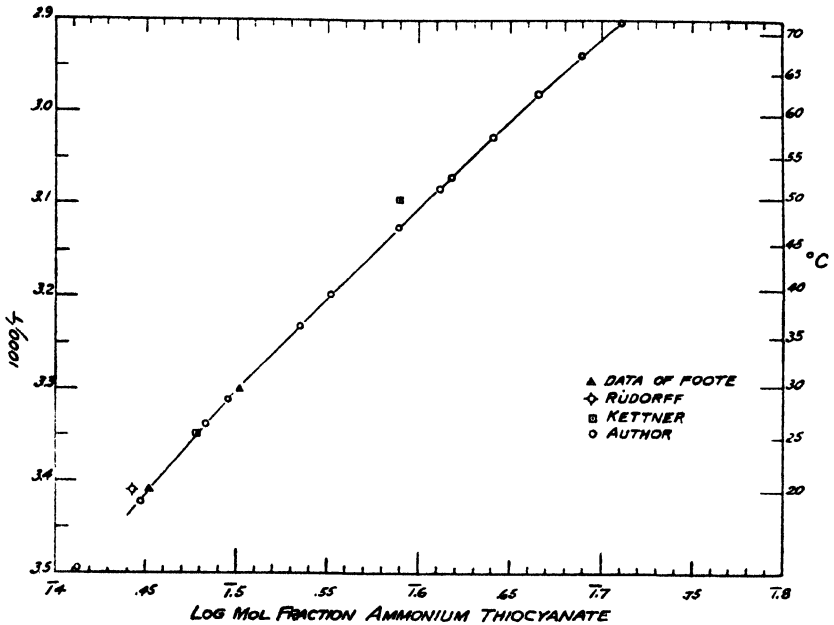

FIG. 1. SOLUBILITY OF AMMONIUM THIOCYANATE IN WATER

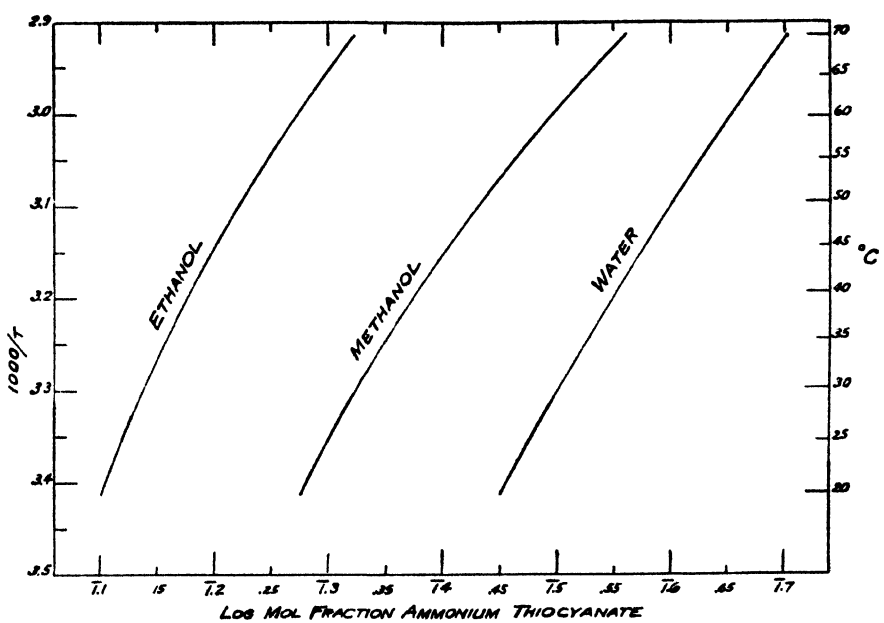

FIG. 2. SOLUBILITY OF AMMONIUM THIOCYANATE IN WATER, IN METHANOL, AND IN ETHANOL

anate in ethanol, it was observed that the tubes as prepared at first were perfectly clear and colorless, but on standing and on exposure to light, in the heating period they turned yellow, and the yellow coloration increased with time. This observation would indicate that some change or reaction between the ammonium thiocyanate and ethyl alcohol was taking place.

SUMMARY

1. A sample of ammonium thiocyanate was carefully purified and analyzed.

2. Some thirteen determinations of the solubility of ammonium thiocyanate in water by the synthetic method in the temperature interval 13 to 72°C. have been made. The precision of measurement in these runs is higher than any previously published.

3. The solubility of ammonium thiocyanate in methanol and ethanol has been determined by the synthetic method from 20 to 70°C.

The author wishes to express his gratitude to Prof. A. A. Sunier for his interest and advice during the progress of this work, and to the Rochester Gas and Electric Corporation for the use of their equipment.

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LIESEGANG PHENOMENON IN SILICIC ACID GEL

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Since the description of rhythmic formation of precipitates by Liesegang (10) in 1896, there have appeared several hundred articles (6) presenting numerous specific examples of this very common phenomenon, as well as many theories to account for the same.

If all salts precipitated uniformly in this manner, the diffusion wave theory of Wo. Ostwald (12) would probably suffice as an explanation. The failure of many compounds to behave in this manner and the numerous irregularities and varieties of periodic structure obtained have led to the propounding of numerous other theories. The theory of Bradford (1) involves the adsorption of the precipitate, that of Holmes (9) emphasizes the part played by the diffusion of the two reactants, and that of Dhar and Chatterji (3) introduces the idea of coagulation and peptization of the precipitate, which was further amplified by Hedges and Henley (7); all these theories are of considerable importance.

The studies on periodic precipitation in silicic acid gels which we have made emphasize the importance of a careful quantitative study of the phenomenon and indicate that a still more comprehensive study is desirable. A number of anomalous formations have been found which are not easily explained by any of the present theories, but not enough data have been assembled to allow an explanation to be attempted. In the present investigation, we have confined ourselves largely to a study of the effect of concentration on the phenomenon, that is, indirectly to a study of the effect of diffusion rate. Only incidentally will reference be made to any of the other factors which have been shown to influence banding. The work is being continued in the hope that sufficient data can be accumulated so that a satisfactory picture of the rôle played by diffusion rates may be formulated.

I. COPPER CHROMATE IN SILICIC ACID GEL

Stansfield (13) has reported the results of his work on the formation of bands of silver chromate in gelatin. His findings showed clearly that the greater the ratio between the concentrations of the salt in the solution and that in the gel, the farther apart were the bands. Although his study was

carefully done, it was felt that with his data available a still more detailed investigation in another system would be of value. The precipitation of copper chromate in silicic acid gel was selected, as it is a very suitable reaction to study.

The silicic acid gel was prepared by mixing sodium silicate and acetic acid solutions. The sodium silicate solution was prepared by dilution of commercial sodium silicate, after settling and filtering, to a specific gravity of 1.060 ± 0.002. Upon titration against standard sulfuric acid, it was found to be 0.60 N ± 0.05. Acetic acid of 1.0 M strength was used, prepared *in situ* as described below.

Test tubes were cleaned with hot chromic acid, then alcoholic sodium hydroxide, rinsed with distilled water, and dried. Into each was introduced with a graduated pipet 0.50 ml. of glacial acetic acid. To each was then added the required volume of standard potassium chromate solution (0.50 M). The volume was then made up with water to 12.5 ml., giving a

TABLE 1

Concentrations of the salt in the gels and of the solutions on top of the gels

CONCENTRATION OF SALT IN GEL	CONCENTRATION RATIOS WHEN THE CONCENTRATION OF THE SOLUTION ON TOP OF THE GEL IS				
	0.5 M	0.4 M	0.3 M	0.2 M	0.1 M
M					
0.01	1:50	1:40	1:30	1:20	1:10
0.03	1:16.7	1:13.3	1:10	1:6.7	1:3.3
0.05	1:10	1:8	1:6	1:4	1:2
0.08	1:6.3	1:5	1:3.8	1:2.5	1:1.2
0.10	1:5	1:4	1:3	1:2	1:1

solution containing the desired concentration of salt and having an acid strength of 0.6 M (in the precipitation of all other salts, 0.75 ml. of acid was used, making a solution of 1.0 M strength). To each tube was then added 12.5 ml. of sodium silicate solution from a graduated pipet. The tubes were then stoppered and inverted. The air bubble was allowed to traverse the tube twenty times. The gels were very slightly basic, and set in about three minutes. After firm gels had been obtained (some hours), 5 ml. of a standard solution of copper sulfate was placed on top of each. The tubes were then tightly stoppered and the reaction proceeded.

In this and most of the following studies, a series of twenty-five tubes was used. The concentration in the gel varied from 0.01 M to 0.10 M potassium chromate, while the concentrations on top were from 0.1 M to 0.5 M copper sulfate. Hence, the values of the concentration ratio lay between 1 and 50. This is more clearly indicated in table 1.

Observations were made daily on these earlier sets of tubes, until the

reaction appeared to be complete. The liquid was then removed from the top and the cork tightly sealed in with shellac. The tubes were preserved practically unchanged for over three years.

A confirmatory series was later prepared by a modified technique which consisted of dissolving the weighed quantities of the salt in the standard acetic acid solution (0.5 *M* in this case). A series of these solutions was made up and 10-ml. portions placed in clean dry test tubes by means of a buret. To each was added 10 ml. of the standard sodium silicate solution and the contents thoroughly mixed as before described. These systems were allowed to stand, and when the gels became firm at the end of about twelve hours, 5 ml. of the other solution was placed on top of each gel by means of a pipet. The tubes were stoppered and allowed to stand.

In figure 1 is shown a series prepared by this modified technique and photographed after about one year. In this the effect of changing the concentration ratio can be seen. The number of bands decreased with the decrease of this ratio, as did also the space between corresponding bands, while the width of the bands increased. Marked irregularities are to be noted. These take the form of spirals in most cases, but well-formed washer-like bands were formed with the small center precipitated at a point slightly farther down the tube.

Stated in another way, as the concentration of the salt in the gel was increased and that on top held constant, the number and spacing of the bands decreased. Keeping the concentration in the gel constant, the effect of an increase in the concentration on top was to cause an increase in the number and spacing of the bands. These effects were noted throughout the entire series studied. Hence it becomes evident that in this case the concentration ratio may be varied by changing the concentration of either salt with exactly the same effect.

II. MERCURIC IODIDE IN SILICIC ACID GEL

This salt was prepared by diffusion of potassium iodide into gels containing mercuric chloride. A series of twenty-five tubes was prepared by the original technique. The concentrations used in the gel were from 0.001 *M* to 0.01 *M*, and those on top from 0.01 *M* to 0.05 *M*. The values used were one-tenth of the usual values, to prevent the formation of a large amount of precipitate, which tends to grow into long needles and obscure the banding.

In figure 2 are shown some of these tubes after reacting two months. The photograph was made three years later. The spacing is not as regular as with other systems. One very distinct effect does stand out, however, and that is that the space between the bands decreases toward the bottom of the tube. This effect has been observed in few other cases. Formation of the soluble double salt $KI \cdot HgI_2$ in the presence of excess potassium

iodide accounts for the absence of precipitate in the upper portion of the tube. Reference to figure 2 shows also that the best bands are obtained when the concentration ratio is highest, and that the distance over which banding occurs is also greatest. This effect is produced by varying the concentration on top. Exactly the same effect is obtained by varying the concentration of mercuric chloride in the gel. This is shown in figure 3.

Dhar and Chatterji describe this salt as one belonging to their second class, and therefore there should be a decrease in the number and spacing of bands with increasing concentration. We find this to be true with increasing concentration in the gel, but not in the solution on top. It is still a question as to whether the effect of potassium iodide in redissolving the precipitate is sufficient to account for this. In the hope of obtaining more information about this system, a new series was prepared by the newer technique described above. Much the same results were obtained. The investigation is being continued.

III. COLLOIDAL MERCURY IN SILICIC ACID

Banding of colloidal mercury was first reported by Davis (2), who reduced mercurous nitrate with sodium formate in agar gel at a temperature of 53°C. Bands were evident, though not good. Orlowski (11) studied the reaction of ammonium hydroxide on mercurous nitrate in gelatin gels. He reports colored layers, followed by remarkable spiral bands. No references have been found to any study of this element in silicic acid gels, nor have either of these reported studies in other gels given any results comparable to the bands formed with common inorganic salts. The results of Davis, if interpreted in the light of some of the theories of banding, point

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FIG. 1. COPPER CHROMATE PRECIPITATES

In these tubes the concentration of the copper sulfate solution was 0.5 *M*, while the concentration of the potassium chromate in the gel was, reading from left to right, 0.01, 0.02, 0.03, 0.04, 0.05, 0.10 *M*.

FIG. 2. POTASSIUM IODIDE-MERCURIC CHLORIDE-SILICIC ACID GEL SYSTEM

The concentration of mercuric chloride in the gel was constant at 0.003 *M*. The concentration of the potassium iodide solution on top of the gel decreased, from left to right, from 0.05 to 0.02 *M*.

FIG. 3. POTASSIUM IODIDE-MERCURIC CHLORIDE-SILICIC ACID GEL SYSTEM

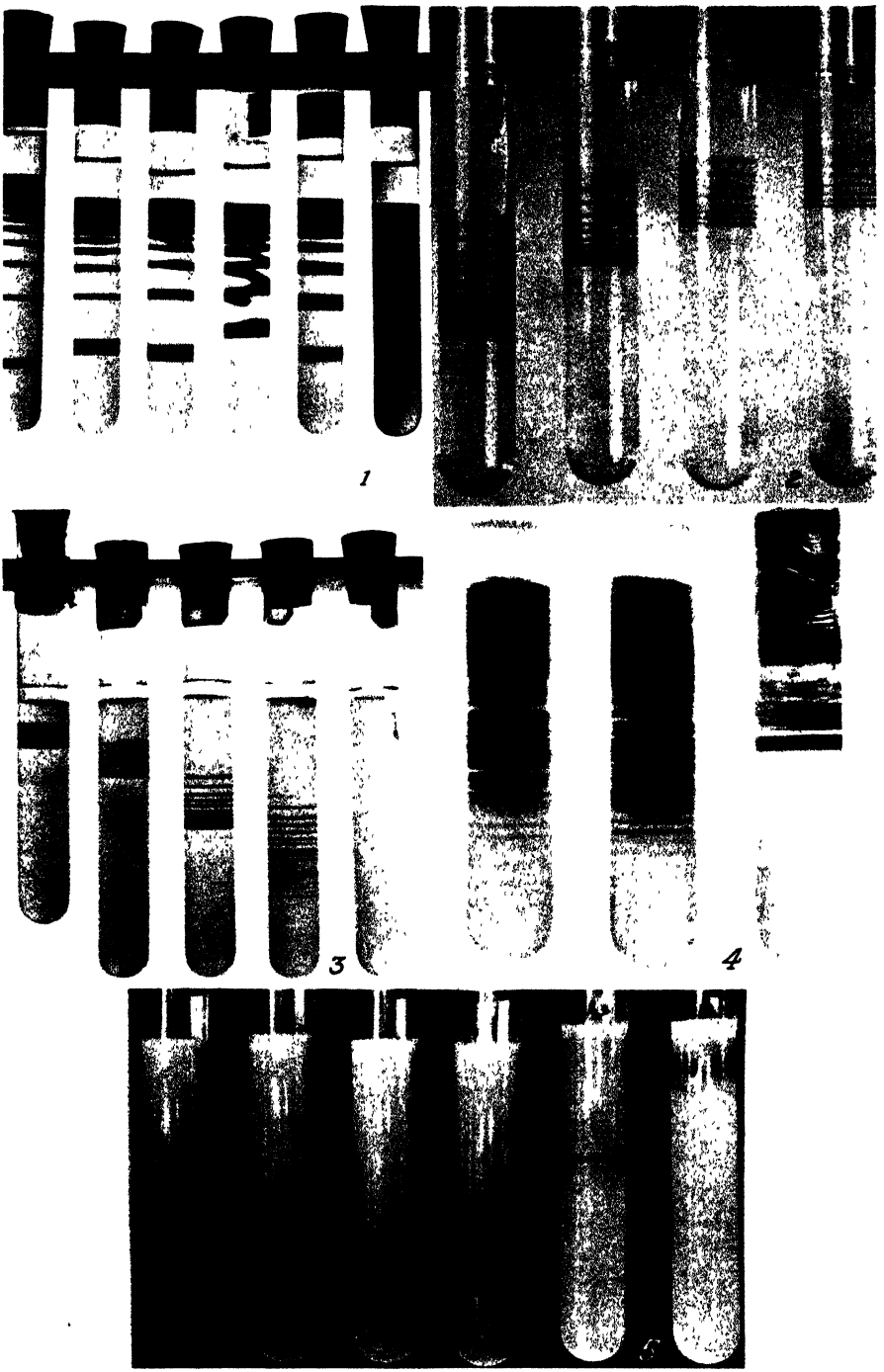
The concentration of the potassium iodide solution on top of the gel was constant at 0.04 *M*. The concentration of mercuric chloride, from left to right, was 0.01, 0.005, 0.003, 0.002, and 0.001 *M*.

FIG. 4. MERCURY-SILICIC ACID GEL SYSTEM

The concentration of the mercuric chloride in the gel was 0.1 *N*. Several portions of 0.2 *N* stannous chloride were used on top.

FIG. 5. LEAD ACETATE-POTASSIUM CHROMATE-SILICIC ACID GEL SYSTEM

The concentration of lead acetate on top of the gel was, from left to right, 0.4, 0.5, 0.4, 0.5, 0.02, and 0.02 *M*. The concentration of potassium chromate in the gel was, from left to right, 0.03, 0.04, 0.04, 0.03, 0.10, and 0.05 *M*.



FIGS. 1–5

toward the possibility of the supersaturation of a colloidal solution for which other evidence is lacking. Further, if the mercury be colloidal, the dispersoid is a liquid; diffusion of this liquid would result in annihilation of any bands which were formed.

We selected the reaction between mercuric chloride and stannous chloride as the most satisfactory procedure. Gels were made as described, except that 3 *N* sulfuric acid was used in place of *N* acetic acid, thus furnishing a strongly acid medium. Thirteen days were required for setting the gel. Saturated mercuric chloride was added to four times its volume of the silicate–acid mixture and 0.2 *N* stannous chloride was employed on top. During thirty-eight days of reaction the stannous chloride was renewed several times.

White bands of what was evidently mercurous chloride progressed down the tube. These later became bands of black mercury and mercurous chloride alternately. Finally, bands of black mercury were all that could be observed. The spaces were very narrow in some parts of the tubes, but very distinct.

These bands are shown in figure 4. The photograph was taken three years later, and the tubes are somewhat damaged by drying. The dense region near the top contains fine bands which do not show in the figure.

Reduction of mercurous nitrate with sodium formate at room temperature proved unsuccessful. Stannous chloride reduced mercurous nitrate to mercury, but without the formation of bands.

IV. LEAD COMPOUNDS IN SILICIC ACID GEL

1. Bands of lead chromate

It is well known that lead chromate and silver dichromate had not until recently been made to band in silicic acid gel. Dhar and Chatterji (4), upon the basis of their theories, attempted to show why these two did not form bands in silicic acid gel. A zone of peptizing values was found inside of which banding did not occur readily. The values for these two salts were believed to lie outside this zone, i.e., the peptizing influence of the gel was too strong to allow banding to occur.

Later, Hatschek (5) showed that silver dichromate could be made to band in silicic acid gel. We have now been able to produce bands of lead chromate in silicic acid gel.

Several series of tubes were prepared by the first technique. After several months reaction they were sealed and preserved. The bands in these tubes were perfectly clear and definite. They were very narrow, and made up of long needles which tended to obscure the bands. For these reasons it was impossible to secure satisfactory definition in photographs of them.

Again, when the concentration in the gel was constant, the distance over

which banding occurred varied directly as the ratio of concentrations. Since in practically all tubes the amount of solution on top was in excess, the constant concentration in the gel should have predetermined a fixed and constant amount of precipitate. The spacing between the bands was wider as the ratio was increased, as found in the other cases reported.

When the concentration on top was held constant (and in excess), the decrease in ratio caused a decrease in the spacing of the bands and in the region in which they were formed. In this case the total quantity of precipitate varies with the concentration in the gel, and is greatest in those tubes in which the distance in which bands were formed is least. Another feature noted throughout the whole series was that bands were closer together near the bottom of the tubes.

It was found difficult to repeat the banding by this technique. The uncertainty of obtaining bands, and their close packing and indistinctness, lend some support to the theory of Dhar and Chatterji that the peptization value for this salt in silicic acid lies near the boundary line. But our observations show that the actual value is probably just within rather than just without the precipitation value.

Later several series of tubes were prepared by the newer technique. The banding was more pronounced and was easy to duplicate. A number of these tubes are shown in figure 5.

2. *Lead iodide*

A series of tubes was made as above, with potassium iodide in the gel and lead acetate on top. The concentration ratios were the same as for lead chromate.

The lead iodide formed large hexagons as usual, but these were arranged in quite definite bands. Measurement of distances was impossible but the banded appearance is unmistakable, as shown in figure 6.

In those tubes in which the concentration of potassium iodide in the gel was less than 0.03 *M* there was no precipitation of lead iodide, although some white crystals appeared in the liquid or imbedded in the surface of the gel. When the concentration reached 0.05 *M*, some crystals appeared in the lower portion of the tube, and it was not until a concentration of 0.10 *M* had been reached that good crystals were formed. The same effects of changing concentration ratio were noted as in the other cases.

By means of the new technique, more series were prepared, and again precipitates occurred in the most concentrated members. Finally, a third series was prepared in which the position of the reactants was reversed. These gave very much better results, forming very large beautiful crystals, but no evidence of bands. This is shown in figure 7. However in all cases the abundance and depth to which the crystals formed was proportional to the increase in the concentration of potassium iodide.

FIG. 6. SHOWING THE BANDED STRUCTURE OF LEAD IODIDE

FIG. 7. LEAD IODIDE IN SILICIC ACID GEL

The concentration of potassium iodide on top of the gel decreased, from left to right, from 0.5 to 0.05 *M*. The concentration of lead acetate was 0.02 *M* in all tubes.

FIG. 8. LEAD BROMIDE IN SILICIC ACID GEL

The concentration of lead acetate on top of the gel, increasing from left to right, was 0.2, 0.3, 0.4, and 0 5 *M*. The concentration of potassium bromide in the gel was constant at 0.05 *M*.

FIG. 9. LEAD SULFATE IN SILICIC ACID GEL

FIG. 10. LEAD FORMATE IN SILICIC ACID GEL

Again, since this was in excess in almost all tubes the amount of precipitate should depend upon the amount of lead acetate present, which was constant.

We conclude from this, that although these crystals grow large and obscure any evidence of bands, one of the factors is still operating, namely that which governs the quantity and distribution of the precipitate. Apparently, either this factor is independent of that which produces the banded structure, or in this case some other factor operates to prevent the formation of small crystals in bands.

3. Lead bromide

Lead bromide has been found to band in gelatin, but in silicic acid gel Holmes (8) reports that under the conditions of his experiments only white twin crystals were formed. We have prepared a concentration series, and among the tubes were found a number exhibiting marked banding. This is shown in figure 8. The bands were, however, almost "opacity" bands, the density of precipitate being very low. It was thought that the potassium acetate formed in the reaction acted to dissolve the lead bromide.

By means of the newer technique, other series were prepared which exhibited only the white twin crystals. Just as in the case of lead iodide, the depth to which the precipitate forms varies directly with the concentration of the solution on top, whereas the quantity should be determined by the much smaller amount of the salt contained in the gel.

4. Lead sulfate

There seems to be no definite information about the precipitation of this salt in silicic acid. We found that a tube containing 0.1 *M* lead acetate in contact with 0.2 *M* ammonium sulfate solution showed excellent bands after two months. One of these tubes photographed three years after it was prepared is shown in figure 9.

Following this a number of concentration series were prepared by the usual method, using potassium sulfate in the gel reacting against lead acetate. There was a marked tendency to band, but the crystals were large and scattered, and the banding was a rhythmic concentration of crystals. The quantity and distribution of the precipitate varied exactly as did that of lead iodide and bromide. Recent experiments show that the use of ammonium sulfate produces much better banding than potassium sulfate.

5. Lead formate

Concentrated formic acid was allowed to diffuse into a gel 0.1 *M* with respect to lead acetate. Nothing at all appeared for several days. Then suddenly, areas of precipitation appeared throughout the tubes, particularly near the bottom. These grew out into long branching masses in a

few hours. During the course of a week these crystals continued to grow, becoming thick and club-like. The reaction was repeated a number of times with similar results. Two of these tubes are shown in figure 10.

This sudden appearance of the precipitate in all parts of the tube at once makes the system of particular interest. Diffusion throughout the whole tube must have taken place with the formation of a supersaturated solution, which suddenly precipitates. Since no evidence of bands can be noted, it appears that this is strong evidence against the precipitation of a supersaturated solution yielding a rhythmic structure, as Ostwald contends.

V. BISMUTH COMPOUNDS IN SILICIC ACID GEL

The citrate, oxalate, iodide, and basic dichromate were prepared in silicic acid gel. No evidence of bands was observed in the case of the first two. Strong citric acid diffusing into a gel $N/25$ with respect to bismuth nitrate gave after several days bunches of crystals resembling cotton and distributed throughout the tube. Supersaturation was again indicated. Saturated oxalic acid diffusing into a gel prepared in the same way gave only tree-like formations of flat, silky crystals.

The basic bismuth dichromate was prepared in a gel formed from two parts of the silicate solution to one of N acetic acid. A small crystal of potassium dichromate was added. The gel set in two minutes and $N/5$ bismuth nitrate was placed on top immediately.

A bright yellow coloration progressed down the tube. Following this, bands of a yellow precipitate formed. They were perfectly plane, well-formed, and very thin. There were many holes in them. In all tubes, five rings formed in a space of about 3 cm.

Potassium iodide diffusing into a gel containing bismuth nitrate produced a heavy reddish brown precipitate. Reversing the reagents gave a yellow ring of color which progressed down the tube. It was followed by a heavy brown precipitate, and finally by well-formed black crystals which appeared to be iodine. A concentration series was attempted, and in every case these black crystals formed, and in many cases grew to be long feathery trees. A great deal of gas was liberated also.

VI. SUMMARY AND CONCLUSIONS

A study of the most favorable ranges of concentration for the formation of banded precipitates of copper chromate, mercuric iodide, mercury, lead chromate, lead iodide, lead sulfate, and basic bismuth dichromate in silicic acid gel has been made. No bands were, however, obtained of lead bromide, lead formate, bismuth oxalate, bismuth citrate, and bismuth iodide.

The pairs of salts were so arranged that in one series one of the pair of reacting salts was in the gel, and in another series the other salt was in the gel. In many cases the results were markedly different.

In all of the salts which were prepared in a concentration series, it was found that if the concentration in the gel was kept constant and that of the solution varied, the depth to which the precipitate formed and the number of bands formed was in proportion to the increase in concentration of the salt in the solution. It was also found that if the concentration in the solution on top was kept constant and that in the gel varied, the depth to which the precipitate formed and the number of bands decreased with the increase in concentration of the salt in the gel.

In general, the width of the bands and the spacing between them increased as the bottom of the tube was approached. We have found two marked exceptions to this, namely, mercuric iodide and lead chromate. Both of these gave numerous bands composed of fine crystals, in which the width of the spaces between the bands decreased toward the bottom of the tube.

It has been found that in those systems in which the concentration ratio was greatest, the banding was best and extended farthest into the tube. In those systems of lower concentration ratios there was rarely any banding.

In addition to this, it was found that in those systems in which banding did not occur, the depth to which precipitates were formed was likewise proportional to the magnitude of the concentration ratio. Therefore it appears that the rate of diffusion, which is approximately proportional to this ratio, is the controlling factor in the distribution of the precipitate.

In the case of lead chloride, lead bromide, and mercuric iodide the additional factor of re-solution of the precipitate by one of the soluble salts seems to be important. The idea that banding is a result of precipitation of a supersaturated solution does not seem to be confirmed by our results on lead formate. The quantitative studies of the concentration relations now in progress in this Laboratory will add some valuable data and we hope will help in the solution of some of these problems.

The interesting phenomenon of the banding of liquid metallic mercury has been recorded.

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PECTIN STUDIES. III

General Theory of Pectin Jelly Formation

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Most of the recent work on the chemistry of the pectin molecule fails to consider that pectins may vary depending upon their source. Even among those who have considered the pectins on the basis of their physicochemical properties, there appears to be a school of thought which favors the view that pectins of whatsoever source are the same and that such differences as are observed are to be considered as due merely to impurities present (6). It has, however, long been recognized commercially that citrus and apple pectins, irrespective of grade, form jellies of definitely different types, although this difference has not generally been recognized in scientific pectin literature.

APPLE AND CITRUS PECTINS

In two earlier papers (7, 11) of the present series the interrelationship of sugar, acid, and pectin was considered for citrus pectin and for apple pectin, respectively.

Whatever the grade of pectin used, the type of jelly obtained remains typical of either citrus or apple. The former jellies are comparatively friable, with little elasticity, while the latter jelly is highly elastic. It is a common observation that apple pectin jellies require—in fact, tolerate—much less acid than citrus pectin jellies similarly prepared. It has also been observed in this laboratory that pectins from other sources, such as cranberry and turnip, differ markedly in their characteristics from either of the above.

THE "OPTIMUM ACIDITY" CONCEPT

A number of explanations of "optimum acidity" as related to pectin jellies have been offered by various investigators since Goldthwaite (3) in 1909 first called attention to the importance of acid. Lal Singh (9) demonstrated that the necessary acid may be reduced by increasing the sugar concentration. However, Tarr (12) and Baker (1) for the first time placed the matter on a definite quantitative basis not only by measuring the acidity in terms of pH but by devising a means for expressing jelly

strength accurately. These authors repeatedly suggested that the optimum acidity indicated a stoichiometric relationship between pectin and acid. Spencer (10) in 1929 insisted that Tarr and Baker's optimum was related to the hot method only. She presented data to show that with a cold method, that is, the mixing at room temperature of a sugar syrup, acid, and pectin solutions, there is observed a minimum acid requirement, but no maximum acid limit. She suggested that the turning point in the jelly strength curve, called "optimum acidity" by Tarr et al., "might simply mean that at this hydrogen-ion concentration the decomposition of pectin begins to predominate over the increased strength due to increased acidity." The present writer has elsewhere suggested that data obtained for citrus pectin do not conform to these interpretations (7), and Cole, Cox, and Joseph (2) have indicated that jelly failures past the optimum acidity may be caused by the increased rate of setting. It appears to the present author that a few simple concepts from colloid chemistry may suffice to explain quite satisfactorily the observed phenomenon.

Kruyt (4, 5) has outlined a concept of the stability factors operating in a system containing the emulsoid agar-agar. His views may readily be translated into terms of pectin, sugar, and acid. Granted that pectin is a negatively charged hydrophilic colloid we may assume the following:

(1) The sugar functions as the dehydrating agent.

(2) The hydrogen-ion concentration functions by reducing the negative charge on the pectin, thereby permitting the pectin to precipitate and coalesce in the form of a network of insoluble fibers, providing the concentration of the sugar is sufficiently great.

(3) The dehydration of the pectin particle by sugar is not instantaneous but requires time to come to an equilibrium.

(4) The rate of dehydration and precipitation increases directly as the hydrogen-ion concentration.

(5) The maximum jelly strength is reached when the system reaches equilibrium, and depends upon the position of that equilibrium.

(6) Any component added to a pectin jelly system, including salts, which causes a change in the ultimate jelly strength of that system may function either (a) by changing the rate of gelation, or (b) by affecting the position of the ultimate equilibrium of the system, or (c) by a combination of these two effects.

In any given jelly mixture the rate of precipitation and orientation of fibers or micellae will go on at a rate varying directly with both sugar concentration and hydrogen-ion concentration and each pectin–acid–sugar combination will have a time limit, inherent in the procedure, at which the jelly structure is so well formed that any mechanical disturbance will reduce the ultimate perfection and therefore the strength of that struc-

ture. It is to be assumed that temperature will be an additional factor in these relationships. On this basis for a given time–temperature–pectin–sugar combination, that is, for any given empirical jelly-making procedure, there must be a maximum hydrogen-ion concentration which results in a rate of gelation that barely permits the completion of the procedure within the time limit of the system. This would be the optimum acidity for that particular combination.

From this viewpoint the changes observed with varying sugar concentrations become logical. The disappearance of an optimum at the lower sugar concentrations simply means that the rate of pectin precipitation has become sufficiently slow at all acid concentrations so that the time factor does not enter. Likewise the absence of an optimum in Spencer's jellies does not distinguish a cold method from a hot method, but simply indicates that she operated within the time limit of the system. In other words, the "optimum pH" may be considered purely manipulative in character and is that hydrogen-ion concentration in any given procedure at which premature gelation becomes a measurable factor in the jelly strength of the finished jelly.

On the above basis we may postulate that: (1) Other types of pectin will show a behavior similar to that of citrus pectin, although not necessarily at the same proportions of sugar and acid. Using the same short-boil empirical method as previously used there should be for each pectin some sugar level at which the rate of jelly formation becomes sufficiently slow so that the so-called optimum disappears. (2) The optimum pH may be made to pass through these same stages by merely changing the time relationship of the process.

APPLE PECTIN

The above postulates were considered in our observations on apple pectins. The experimental procedure was identical with that previously described (7). In order to obtain a greater variation in acidity, phosphoric acid was used instead of tartaric acid. The acid was added in the form of a 25 per cent solution, allowance being made for the amount of water thus added. The pH of the finished jelly was determined by the quinhydrone method (11). The apple pectin used, 119F, is an alcohol-precipitate from Certo. Details of procedure and the results obtained appear in table 1 and figure 1. It may be noted that although the characteristics of this pectin are definitely different from those previously shown for citrus pectin, nevertheless a sugar concentration can be found in each case at which the rate of gelation is such that no definite optimum is shown. For 119F this is at 50 per cent sugar. The 60, 55, and 50 per cent curves for 119F resemble respectively the 70, 65, and 60 per cent curves previously shown for citrus pectin. This is in agreement with postulate 1.

TABLE 1

Effect of sugar concentration on "optimum acidity" and jelly strength of apple pectin jellies (119F alcohol-precipitated pectin)

All series of jellies identical except for sugar concentration. 2.5 g. of pectin 119F and the indicated amount of acid was used. Final net weight of jelly 555 g. Total heating time, about 4¾ minutes. See also figure 1.

25 PER CENT PHOSPHORIC ACID PER BATCH OF JELLY	SUGAR CONCENTRATIONS							
	50 per cent		55 per cent		60 per cent		70 per cent	
	J.S.*	pH	J S.	pH	J.S.	pH	J.S	pH
cc								
0.15	—	—	—	—	0	3.34	50	3.62
0.25	—	—	—	—	—	—	65 66	3.40 3.35
0.30	—	—	—	—	11.5	3.21	60	3.27
0.35	—	—	—	—	—	—	62	3.24
0.40	—	—	—	—	40	3.06	55†	3.09
0.50	—	—	11	2.87	63	2.92	[32]	2.93
0.55	—	—	—	—	61	2.81	—	—
0.60	5	2.67	—	—	57	2.74	—	—
0.70	—	—	43	2.61	—	—	—	—
0.80	—	—	47 51	2.53 2.50	39	2.46	—	—
0.90	18 5	2.41	51	2.42	—	—	—	—
1.00	—	—	42	2.39	39.5	2.34	—	—
1.20	21.5	2.22	—	—	—	—	—	—
1.40	—	—	34‡	2.26	29	2.16	—	—
1.50	31	2.12	—	—	—	—	—	—
1.60	—	—	27	2 10	21	2.02	—	—
1.80	—	—	25 5	1.98	—	—	—	—
2.00	26	1.98	21.5	1 94	[12]	1 92	—	—
2.50	26	1.83	—	—	—	—	—	—
3.00	31	1.79	24.7	1 73	—	—	—	—
3.50	27	1.72	—	—	—	—	—	—
4.00	27.5	1 66	—	—	[11]	1.62	—	—
5.00	27	1 59	32	1 61	—	—	—	—
10.00	33	1 37	36 5	1.37	[9]	1.20	—	—
35 00	31	1.05	31§	0.86	[9]¶	0.98	—	—

* Jelly strength.
† 0.42 cc. of acid.
‡ 1.3 cc. of acid.
§ 40 cc. of acid.
¶ 30 cc. of acid.
Figures in brackets indicate "curdled" jellies.

It becomes apparent from a study of these curves that for most practical purposes jellies containing 60 to 65 per cent sugar should be preferable. In all cases the further lowering of sugar concentration carries the penalty of

lower jelly strength and greater acid requirement. This lowering of jelly strength may be assumed to be due to incomplete dehydration and therefore either incomplete precipitation or a more flexible network of pectin.

THE TIME FACTOR CONCEPT

The second postulate made above was first tested by preparing jellies in the manner suggested by Spencer, except that the temperature of the jelly mixture was 55°C. instead of room temperature. This allows a greater time factor without involving any measurable hydrolysis of the pectin. The jellies made were 60 per cent. The pectin used was the 119F used in previous observations and the amount used identical with the prior series.

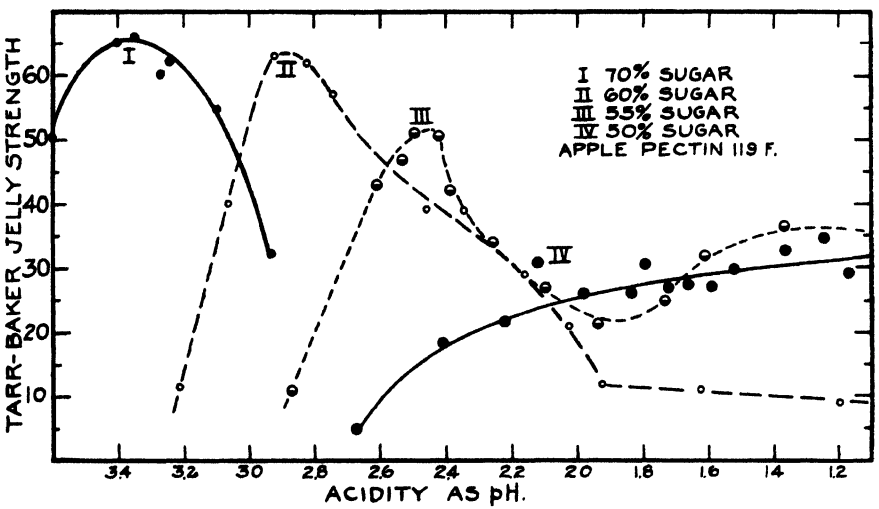

FIG. 1. EFFECT OF SUGAR CONCENTRATION ON OPTIMUM pH AND JELLY STRENGTH OF APPLE PECTIN JELLIES

Phosphoric acid used

The 2.5 g. of pectin and 30 g. of sugar were dissolved in just enough water to make a total of 140 g. and brought to 36°C. The sugar, the minimum amount of acid used, and the remaining water were boiled together, cooled to 65°C., and adjusted to correct weight with distilled water. The additional acid was then added and the pectin solution rapidly stirred in while the beaker remained immersed in a water bath at 55°C. The temperature of the jelly mixture was in each case 55°C. Allowance was made in all weights for the amount of pectin solution remaining in the original beaker.

Three series of jellies were made, varying the acid within the same limits used in previous series. For series A the total mixing time from the moment the pectin solution was poured into the warm syrup until the mix-

ture was poured into the glasses was exactly 8 seconds; for series B the time was 50 seconds; for series C the time was 90 seconds. The results in every way conformed to the postulate made. The magnitude of the jelly strength for the 8-second series was quite remarkable, indicating that under the conditions of the usual hot method even at the optimum point only a fraction of the true jelly strength is obtained. The results are listed in table 4 and are shown graphically in figure 2 along with the corresponding 60 per cent curve from table 2. There is also shown a curve obtained in a manner identical with the latter except that an additional 80 cc. of distilled water was added to each batch of jelly, thereby changing the heating

TABLE 2

The relation of the time factor to optimum acidity

The time indicated is the interval between the pouring of the pectin solution into the sugar syrup and the pouring of the mixture into the glasses. Jellies contain 60 per cent sugar, 2.5 g. apple pectin 119F, phosphoric acid as indicated. Temperature of pectin solution, 36°C.; of sugar solution, 65°C.; of final mixture, 55°C.

25 PER CENT PHOSPHORIC ACID	SERIES B 90 SECONDS		SERIES C 50 SECONDS		SERIES D 8 SECONDS	
	J S.	pH	J S	pH	J S	pH
cc.						
0.26	—	—	0	3.27	—	—
0.36	33	3.10	—	—	36 5	3 13
0.56	69	2.80	—	—	67	2 88
0.86	—	—	80	2.50	—	—
0.96	41	2.39	—	—	115	2 40
1.06	—	—	75	2 37	—	—
1.26	—	—	61.5	2.24	—	—
1.56	19	2.13	—	—	120	2.13
1.96	14.5	2 03	28 5	2.00	145 (?)	2.01
3.96	—	—	—	—	135	1.76

time from $4\frac{3}{4}$ to 10 minutes. The final net weight was the same in all cases.

One may consider the data shown in figure 2 as those of five investigators using methods A_1, A_2, B, C, and D in their individual studies of the same pectin 119F. It is apparent that A_1 and A_2 would conclude that this particular pectin had an optimum pH of either 2.96 or 2.90. B would place the optimum for the same pectin near pH 2.8, and C about pH 2.6, while D would conclude that the maximum jelly strength is not reached without sufficient acid to give a pH of 2.0 or less, and that apparently we cannot have too much acid.

It still remains true, however, that *with any given procedure* the acid relationship of each type of pectin is a definite characteristic which must

be carefully considered in order to obtain best results. Evidently the factor which is most involved is the rate of gelation of the pectin as affected by the acid. The largest or "optimum" amount of acid to be used will be that point at which an additional increase of acid will increase the rate of setting to a point where loss in jelly strength due to a disturbance of the jelly in the stirring or pouring exactly balances the strengthening effect of that same increment of acid. Such observations emphasize the necessity for close adherence to a given empirical method of jelly making in any systematic study of the factors involved.

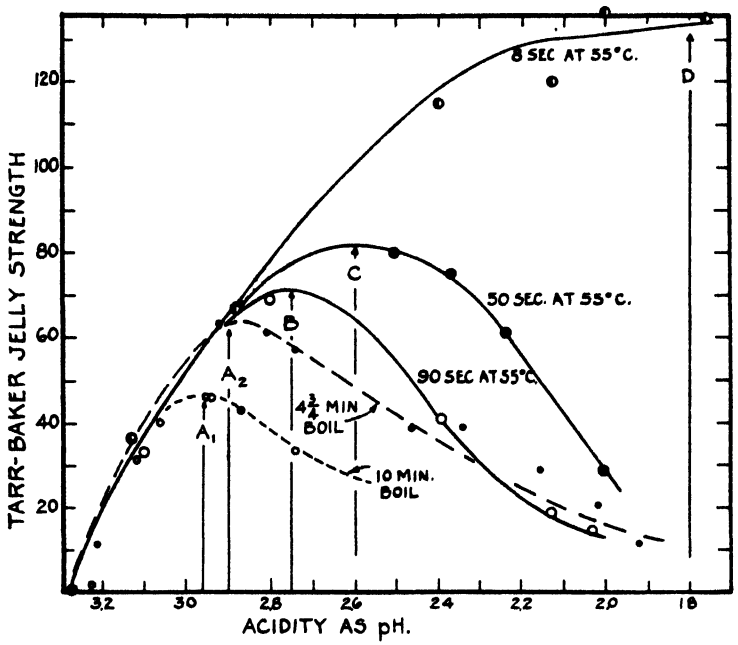

FIG. 2. EFFECT OF METHOD OF MAKING JELLY UPON "OPTIMUM ACIDITY"

60 per cent sugar; apple pectin 119F; phosphoric acid

THE TEMPERATURE FACTOR

The abnormally high jelly strengths obtained at 55°C. cannot be explained on the basis of the time concept. Apparently the usual high temperature of jelly making either destroys a large proportion of the pectin value, or the character of the gel structure obtained at the lower temperature differs from that formed from a hot mixture.

For a number of years it has been a common commercial procedure to place the acid solution in the container into which the non-acidified pectin–sugar–water mixture is subsequently poured. This practice was shown by Stuewer, Beach, and Olsen (11) to eliminate the so-called optimum peak

when the jellies were poured at 96°C. The mixing by pouring is almost instantaneous, but the jelly strengths did not differ greatly from those observed at optimum using the regular method. On the basis of the time factor curves shown in figure 2, it did, however, seem reasonable to expect that this method, which permits of maintaining mixing time at a minimum, should show a rise in jelly strength as the temperature of pouring is lowered from 100°C. to room temperature. Accordingly several double batches of non-acidified pectin jelly mixtures were prepared by the usual hot method. After quickly cooling the mixtures to a desired temperature, with proper adjustment for loss in evaporation, the syrup was poured into a

TABLE 3

Effect on jelly strength of preparing jelly mixture without acid, cooling to different temperatures, and pouring into glasses containing varying amounts of acid

60 per cent sugar; 2.5 g. of 119F pectin in 555 g. of jelly; acid as indicated

GLASS NO.	10 PER CENT PHOSPHORIC ACID	WATER	JELLY STRENGTH AND pH VALUES OF JELLIES POURED AT THE FOLLOWING TEMPERATURES														REGULAR PROCEDURE	
			100°C.		90°C		80°C		70°C		60°C.		50°C.		40°C			
			J.S.	pH	J S.	pH	J S	pH	J.S	pH	J.S	pH	J S	pH	J.S.	pH	J S.	pH
	cc.	cc.																
1	0	2.0	0	3.66	—	—	—	—	—	—	—	—	—	—	—	—		
2	0.20	1.80	13	3.11	19	3.09	14	3.12	14	3.13	13.5	3.21	—	—	—	—		
3	0.30	1.70	38	2.94	37	2.85	40	2.84	45	2.89	35	3.00	—	—	—	—	34.5	2.83
4	0.40	1.60	39	2.74	36	2.70	32?	2.68	42	2 62	47	2.68	64	2.73	69	2.85	37+	2.68
5	0.60	1.40	42	2.38	45.5	2 35	43	2.48	40	2.40	45	2.42	86	2 33	85	2.58	31.5	2.52
6	0.80	1.20	38	2.23	47	2.23	45	2.23	46	2.25	59	2.19	80	2.31	92	2.35	25	2.31
7	1.0	1.0	38	2.14	57	2.11	48.5	2.11	55	2.15	64.5	2.15	76	2.19	100	2.18		
8	2.0	0	35	1.85	48	1.86	49	1.89	62	1.85	65	1 89	97	1.88	93	1.88		
8a	2.0	0	40	—	49	—	52	—	—	—	—	—	86*	—	—	—		
8b	2.0	0	40	—	—	—	—	—	—	—	—	—	—	—	—	—		

* 55°C.

series of eight glasses containing varying amounts of 10 per cent phosphoric acid solution plus water to make 2 cc. Rapid pouring results in efficient mixing of acid, no stirring being necessary; in fact at the lower temperatures the "set" was so rapid that stirring was not desirable.

The results are given in table 3 and figure 3. The figures obtained are rather irregular. It should be noted, however, that each point plotted on the graph represents only one measurement on one glass of jelly, while usually such points represent the average of four jellies. Considerable variation was therefore to be expected. Nevertheless, the trend of these results is quite apparent, and it can be stated that repeated tests with other samples of apple pectin invariably showed similar differences in jelly strength between jellies poured at varying temperatures.

It remained to determine whether the low jelly strengths obtained at 100°C., as compared with the high values obtained at 50°C., were due to acid destruction of the pectin at the higher temperature or to a tendency of the pectin to set differently from a hot solution than from a cool solution. In this connection it should be borne in mind that the very rapid setting at 50°C., compared with the somewhat slow set of jellies poured at 100°C., is unfavorable to uniform mixing of the acid and jelly mixture at the lower

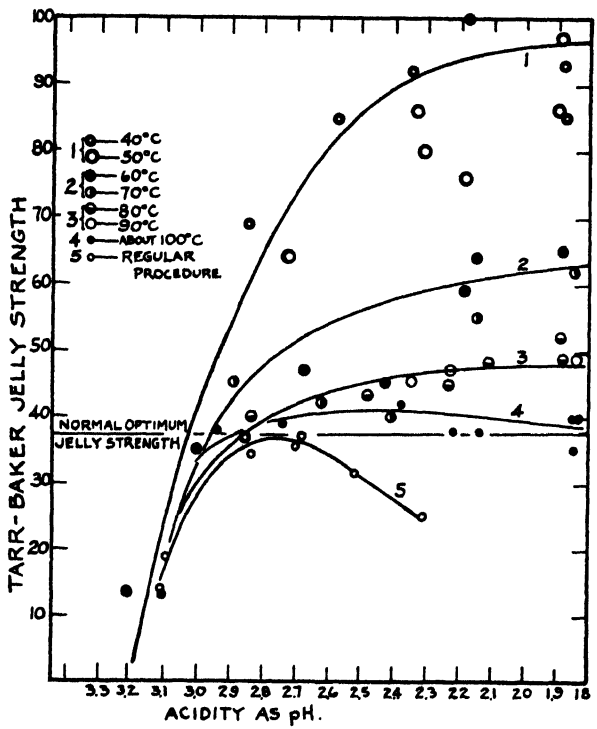

FIG. 3. EFFECT OF TEMPERATURE AND METHOD OF PREPARING JELLIES UPON SO-CALLED OPTIMUM pH AND MAXIMUM JELLY STRENGTH OF APPLE PECTIN 33F

temperature. One might, therefore, logically expect a less perfect jelly at the lower temperature.

This question was answered by recovering the pectin from duplicate batches poured (a) at 100°C. and (b) at 50°C. and remaking the recovered pectin into jellies, both of which were poured at 50°C. This procedure was repeated. In each case the pectin from the low-strength jelly when remade into the same amount of jelly at 50°C. gave a jelly strength practically equivalent to that obtained with pectin recovered from the high-strength jelly. This is conclusive proof that the lower strength of the

jellies prepared by pouring at 100°C. is not due to hydrolysis of the pectin by the acid. Evidently the rapid set at the lower temperatures results in a different and stronger gel structure. This is contrary to experience with gelatin, where it was found that slow setting at a higher temperature resulted in better jelly formation than quick setting at low temperatures (8).

It was thought of interest to determine whether in the course of time jellies identically prepared, except for the temperature of pouring, would tend to approach the same equilibrium in jelly strength. Results indicate the contrary. Observations over a period of four weeks show the high-strength low-temperature jellies to increase in strength at a more rapid

TABLE 4

The effect of temperature of contact with acid upon jelly strength and upon pectin grade

NO	TEMPERATURE OF POURING	JELLY STRENGTH*	JELLY STRENGTH WITH RECLAIMED PECTIN (POURED AT 50°C.)*
	°C		
1	100	53	90
2	50	118	98
3	100	55	112
4	50	132	135

NO.	TEMPERATURE OF POURING	JELLY STRENGTH†				
		1st day	3rd day	8th day	2 weeks	4 weeks
	°C.					
5	100	35	39	43	42	43
6	50	87	116	115	131	122

* Each figure the average of four determinations.

† Each figure the average of two determinations.

rate than the low-strength jellies poured at 100°C. These results are tabulated in table 4. The details of the experiments were as follows:

Five grams of pectin, 800 g. of sugar, and 545 cc. of water were brought to a boil in the usual manner and cooked to a net weight of 1313 g. From this batch four glasses, each containing 2 cc. of 10 per cent phosphoric acid, were filled at 100°C. (total, 555 g. of jelly). The remaining syrup was cooled rapidly to 50°C., adjusted for loss by evaporation, and four glasses, each containing 2 cc. of 10 per cent phosphoric acid, were filled at that temperature. The extra syrup was discarded. After standing overnight the jelly strength was determined and identical amounts of each batch (as nearly 555 g. as possible) were cut into small pieces and steeped in 60 per cent alcohol. The alcohol was changed three times in the course of that many days. Finally the pectin jelly was drained on a cloth,

washed with strong alcohol, squeezed dry, and at once dissolved in sufficient water for the preparation of a standard batch (555 g.) of jelly. These jellies were both poured at 50°C. The entire procedure was subsequently repeated.

The results throw an interesting light upon the pectin gel formation. Apparently the structure of the jelly is fundamentally different when slowly set from the hot solution than when rapidly set from the cool syrup. If we assume that pectin exists in two states of hydration, that is, if the amount of water bound by the pectin fibrils differs depending upon the temperature at which the pectin is precipitated, then a ready explanation is at hand.

Summing up the entire thesis one may say that in the ideal pectin jelly system each increment of acid functions in two ways, although these fundamentally may be counterparts of the same function: first, the rate of gelation is increased towards a maximum; second, the strength of the ultimate gel structure is increased towards a maximum. When in any system the time factor does not interfere with the maximum rate there will be no optimum acidity (curve D). If, however, at some point the rate of gelation crosses the time boundary of the system, that point will be the optimum for that system because further increases in rate of gelation will be increasingly interfered with until the maximum rate of gelation is reached, at which point further increments of acid will not cause any further change. The latter accounts for the flat portion of the curves in figure 1 of the present paper and in figure 1 of Pectin Studies I (7). It is apparent that anything that may change the rate of gelation will change the position of the optimum in any given system.

SUMMARY

A colloid theory to explain the process of pectin jelly formation is formulated. It is shown that it assists in explaining and to some extent anticipating the behavior of different types of pectin.

On the basis of this theory it is postulated that the so-called "optimum hydrogen-ion concentration" of jelly making may be varied by changes in time, the same as it is through changes in sugar concentration. Experimental data supporting this thesis are presented.

The effect of any substance added to a pectin jelly system which registers as a change in jelly strength of that system may be due to (a) an effect on the rate of gelation, or (b) an effect on the ultimate jelly structure, or (c) a combination of these two.

It is shown that apple pectin jellies rapidly prepared at 55°C. have abnormally high jelly strength as compared with jellies prepared by the short-boil method, indicating that only a fraction of the true jelly strength is obtained by the usual methods of preparing jellies.

Data presented show that the original amount of pectin is recoverable

unchanged from jellies prepared either at 50°C. or at 100°C. This proves that the difference in jelly strength is due not to pectin destruction at the higher temperatures but to structural differences in the pectin network forming the jelly. It is suggested that the amount of water bound by the precipitated pectin may differ depending upon the temperature at which the precipitation occurs.

Acknowledgment is due W. VanCamp and J. S. Kemp for assistance in the preparation of the jellies and in the determination of pH and jelly strengths.

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THE COMPRESSIBILITY COEFFICIENTS OF SOLUTIONS OF EIGHT ALKALI HALIDES

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Although the compressibility coefficients of aqueous solutions have been determined by several investigators,[1] there exist at present no comparable measurements of this property for a series of solutions of related substances. As a preliminary step to fill this need, the compressibility coefficients of a number of solutions for each of eight alkali halides have been determined at 35°C. over the pressure range 100 to 300 metric atmospheres (megabars). The solutions measured were prepared from purified materials; their composition and density were also measured with considerable precision.

PURIFICATION OF MATERIALS

The general reagents used in the purification of the salts may be described briefly. Water was doubly distilled, once from alkaline permanganate and then once from dilute sulfuric acid with the use of tin condensers. Constant boiling hydrochloric acid and hydrobromic acid were obtained by distillation through a quartz condenser.

The starting material for the preparation of lithium chloride and bromide was lithium carbonate of C.P. grade. The carbonate was first washed repeatedly with water until there was no test for halogen, and was then converted to the chloride or bromide by solution in the halogen acid. In order to precipitate any basic impurities a slight excess of carbonate was left at the end of the solution. After boiling the solution the residual carbonate was filtered off. The solution containing the halogen salt was then evaporated until a crop of crystals formed on cooling the solution in ice. These crystals were collected and were drained with the aid of a centrifuge. This crystallization operation was repeated until about two-thirds of the salt in solution was obtained in the form of crystals.

The sample of sodium chloride used was some left over from an atomic weight determination and was of a very high degree of purity. Pure sodium bromide was obtained by a single crystallization of the C.P. salt

[1] Literature references to work before 1923 are given in the International Critical Tables, Vol. III, p. 439. Measurements reported since 1923 are given in references 1, 2, and 6.

from water with centrifugal drainage. Sodium iodide which had been synthesized from pure sodium oxalate and iodine was available from a previous research.

Potassium chloride was precipitated once from aqueous solution by conducting hydrogen chloride gas to the surface of the solution. Centrifugal drainage was used to separate the salt from the mother liquor. The potassium bromide and potassium iodide were purified in exactly the same manner as sodium bromide.

PREPARATION OF SOLUTIONS AND THEIR DENSITY DETERMINATIONS

One stock solution of lithium chloride and two of lithium bromide were prepared by dissolving the salts in an almost minimum amount of water.

TABLE 1

Analysis of lithium halide solutions

(All weights reduced to vacuum standard)

SOLUTION	WEIGHT OF SAMPLE	WEIGHT OF AgX	WEIGHT PER CENT OF LiX IN SOLUTION
	grams	*grams*	
LiCl	3 10328	4 41553	42 086
	3 16457	4 50251	42 084
			Av. = 42 085
LiBr (solution I)	3 36461	4 39467	60.410
	3 76652	4 91968	60.409
			Av. = 60.410
LiBr (solution II)	3 93692	4 66161	54.764
	3 92118	4 64256	54.759
			Av. = 54 761

The halogen content of these solutions was found by precipitation with silver nitrate and weighing as the silver halide. The results of these analyses, which were carried out with great care, are given in table 1. The other solutions of these salts were prepared by dilution of weighed portions of these stock solutions.

The solutions of the sodium and potassium salts were prepared by dissolving a weighed amount of the salt in water and then determining the weight of the resulting solution. This procedure was adopted because, according to Baxter and Wallace (3), the sodium and potassium salts can be thoroughly dried without danger of decomposition. The two chlorides were fused in platinum vessels previous to weighing. The bromides and iodides, however, were heated in platinum only to 250°C. After two hours of heating these salts were powdered by gentle grinding in an agate mortar

and the heating continued for another two-hour period. After a second grinding the salts were subjected to a final heating of at least three hours prior to weighing. It may be noted here that a few of the dilute solutions of these salts were prepared by dilution of weighed samples of the more concentrated solutions. These cases will be indicated in the table of results (table 3). Immediately after their preparation all the solutions were transferred to Pyrex glass-stoppered bottles. To prevent loss by evaporation during storage, each bottle was covered with a bottle cap held by a rubber collar which fitted tightly around the neck of the bottle.

The density flasks were ordinary 100-cc. graduated flasks, the necks of which had been constricted to about 3 mm. at the point of graduation to secure greater accuracy in setting the meniscus. The volumes of these flasks at 35°C. were found by dividing the vacuum weight of their water content by the density of water at that temperature (0.99406). To determine the density of a salt solution, the weight in vacuo of that amount of solution which filled a flask to the graduation was found and divided by the volume of the flask.

The following observations will complete the foregoing description of the preparation of the solutions and their density determinations. All weighings were made with calibrated weights on the same balance. Whenever flasks were involved, suitable counterpoises were employed. Precautions were always taken to insure that the surfaces of the flask and counterpoise were subjected to the same treatment. All weighings were reduced to vacuum standard by the usual formula. The thermostat employed in the density measurements was the same one used in the compressibility experiments and will be described in more detail later. To bring the density flask and its contents to the desired temperature the flask was immersed in the thermostat and allowed to remain there for at least two hours before the final adjustment of the meniscus. This adjustment was accomplished in two ways. If the composition of the solution had already been established, the adjustment was made by means of fine capillaries. In some instances, however, the weight of the solution in the density flask served also as the final weight in the determination of the composition of the solution by dilution. In these cases the meniscus was adjusted either by addition of water or by evaporation by passage of a current of dry filtered air over the surface of the meniscus.

Since the weight of a solution in the density flask was always greater than 100 g. and was determined to the nearest milligram, the precision of the density measurements is at least one part in 50,000. Check measurements were not made as a rule, but the occasional ones, using different flasks, agreed well within the above estimate. The flasks were again calibrated after being in use for a year and showed no appreciable change. The precision of the weight per cent composition of the solutions varies some-

what with the method of preparation and diminished with decreasing concentration. The uncertainty in this quantity is probably less than one part in 10,000.

THE DETERMINATION OF THE COMPRESSIBILITY COEFFICIENTS

These measurements were made by the method in use in the Harvard Laboratory. Since this method has been described fully in other papers (7), it will be necessary to give here only the more important details bearing on the present experiments.

The compression pump, which was manufactured by A. L. Henderer's Sons, was connected with the compression cylinder and the pressure gage. This gage was of the absolute type, in which pressures are measured by an oscillating piston weighted with carefully standardized weights. A piston with an accurately known area (0.31619 cm.^{2}) was loaned to us for this work. The piezometer was the one used by Dr. B. J. Mair and Miss E. H. Lanman in their experiments (5a). It was constructed of glass and was provided with a solid glass stopcock which was removed in order to fill the vessel. The piezometer had a volume of about 34 cc. and in an experiment it contained, as a rule, approximately 31 cc. of solution and 3 cc. of mercury.

The compression cylinder was mounted in a large thermostat which has already been described (9). It was possible to regulate the temperature of the bath so that the maximum variation was less than 0.005°C. The temperature of the bath was 35.00°C., established by means of a mercury thermometer certified by the Bureau of Standards.

The compressibility coefficients were calculated by use of the usual equation

$$\beta = \frac{(w_2 - w_1)D}{d \cdot 200 \cdot W} + \beta'$$

where

W is the weight of solution contained in the piezometer;

w_1 is the weight of mercury needed to compensate for the volume change produced by changing the pressure from 100 to 300 megabars when the piezometer is filled with mercury;

w_2 is the weight of mercury needed to compensate for the volume change produced by changing the pressure from 100 to 300 megabars when the solution is filled with W grams of solution and mercury;

D is the density of the solution at 35°C. and at atmospheric pressure;

d is the density of mercury at 35°C. under 300 metric atmospheres pressure (13.525);

β' is the compressibility coefficient of the reference substance, mercury, and was assumed to be 4.00×10^{-6}; and

β is the average compressibility coefficient over the pressure range 100 to 300 metric atmospheres of the substance in the piezometer.

In determining the values of w_1 and w_2 the following procedure suggested by Mair and Lanman was adopted. The amount of mercury in the piezometer was adjusted at the outset so that the electrical contact through the platinum wire–mercury interface was broken when the applied pressure was very close to 300 megabars. After the exact pressure was measured, mercury was removed from the piezometer until the pressure necessary to break the contact was approximately 100 megabars. Following exact determination of this second pressure, the mercury, which had been with-

TABLE 2

Data and calculations for the compressibility coefficient of sodium iodide solution No. 4

	EXPERIMENT I	EXPERIMENT II
Weight of piezometer, mercury, and solution (grams)	134 386	134 324
Weight of piezometer and mercury (grams)	100 136	100 015
Weight of solution in air (grams)	34 250	34 309
Vacuum weight of solution (W) (grams)	34 282	34 341
Density of solution	1 10998	1.10998
Weight of mercury removed (grams)	3 2023	2 8964
High pressure point* (megabars)	306 32	292 09
Low pressure point (megabars)	95 38	101 71
Check high pressure point (megabars)	306 38	292 11
Accepted high pressure point (megabars)	306 35	292 10
w_2 (grams)	3 0358	3.0426
w_1 (grams)	0 1500	0 1500
$\beta \times 10^6$	38 54	38 56
Accepted value of $\beta \times 10^6$	38 55	

* Pressure in megabars equals $\frac{\text{weight on gage} \times \text{acceleration of gravity}}{\text{area of piston} \times 10^6}$ where weight on gage includes weight on platform plus weight of platform; acceleration of gravity is 979.272, and area of piston was 0.31619 cm^2.

drawn and in the meantime weighed, was now returned to the piezometer and the initial pressure checked. The values of w_1 or w_2 corresponding to exactly 200 metric atmospheres were calculated by direct proportion from the weight of mercury removed and the pressure difference which covered very closely the range 100 to 300 megabars.

Certain points with regard to the routine of the experiments should perhaps be noted here. Following the recommendation of Cohen and Schut (4), the capillary tube below the platinum contact was allowed to become moistened with water before the initial pressure application in each experiment. The practice was adopted of completing the pressure de-

TABLE 3

Table of results

SOLUTION	WEIGHT PER CENT OF SALT	DENSITY	$\beta \times 10^6$	AVERAGE DEVIATION
Lithium chloride solutions				
1 (ds)	42 031	1 26364	20.12	0 05
2 (ds)	34.898	1 20970	22 61	0.01
3 (ds)	26 021	1.14836	26.14	0 03
4 (ds)	23 010	1 12896	27 41	0 02
5 (ds)	18 969	1.10418	29 06	0 03
6 (ds)	16 279	1 08776	30 52	0 00
7 (ds)	9 6550	1 04943	34 45	0 01
8 (ds)	4.1221	1 01772	38 35	0 00
Lithium bromide solutions				
1 (i)	60 410	1 72090	22 37	0 02
2 (i)	54 761	1 60856	24 13	0 01
3 (d1)	49 949	1 52364	25 69	0 05
4 (d1)	45 438	1 45294	27 09	0 03
5 (d2)	43 493	1 42456	27 70	—
6 (d1)	36 696	1 33423	29 46	0 02
7 (d2)	31 897	1 27784	30 94	0 02
8 (d2)	25 388	1 20827	32 92	0 03
9 (d4)	17 229	1 13097	35 50	0 00
10 (d2)	12 959	1 09397	37.17	0 02
11 (d2)	8 6052	1 05845	38.57	0 01
Sodium chloride solutions				
1 (i)	24.8200	1 17942	27 10	0 01
2 (i)	16 9863	1 11690	30.99	0 03
3 (i)	9 1598	1 05852	35 56	0 01
4 (d1)	6 1298	1 03671	37 54	0 02
5 (d2)	2 8661	1 01388	39 71	0 03
Sodium bromide solutions				
1 (i)	49 295	1.54400	23.42	0 03
2 (i)	32.380	1.30294	29 74	0 03
3 (i)	20 7701	1.17443	34 03	0 00
4 (i)	9 8333	1.07392	38.10	0.02
Sodium iodide solutions				
1 (i)	60 802	1.80644	24 22	0.01
2 (d1)	40.413	1.42173	31 39	0 01
3 (d1)	22.712	1.19758	36.36	0 03
4 (d2)	13.896	1 10998	38 55	0 01

TABLE 3—*Concluded*

SOLUTION	WEIGHT PER CENT OF SALT	DENSITY	$\beta \times 10^6$	AVERAGE DEVIATION
Potassium chloride solutions				
1 (i)	26 522	1 17419	29 64	0 02
2 (i)	17 2876	1 10725	33 35	0 04
3 (i)	7 4440	1 04118	37 83	0 02
Potassium bromide solutions				
1 (i)	40 058	1 36525	29 51	0 01
2 (i)	32 576	1 27822	31 72	0 15
3 (i)	22 985	1 18086	34 68	0 04
4 (i)	10 452	1 07209	38 54	0 04
Potassium iodide solutions				
1 (i)	58 262	1 68149	27 74	0 16
2 (i)	34 901	1 32072	34 22	0 12
3 (i)	16 415	1 12576	38 44	0 17
4 (d2)	8 9594	1 06226	40 04	0 02
5 (d1)	4 4120	1 02648	40 87	0 04

termination fifteen minutes after the initial application of pressure. Further, in a pressure determination sufficient pressure was applied first to just break the electrical contact between the mercury in the piezometer and the platinum wire in the capillary. The pressure was then gradually reduced until contact was just made and the pressure corresponding to this point was the one accepted.

The value of the piezometer constant w_1 was found to be 0.1500 g. from eight different experiments made over a period of one year. Mair and Lanman found w_1 to be 0.1473 g. for the same piezometer at 25°C. The 2 per cent difference is a reasonable figure for the change in the compressibility of the glass and mercury for the 10°C. change in temperature.

In the table of results (table 3) will be given only the final calculated values of the compressibility coefficients for the solutions. To illustrate both the experimental procedure of the compressibility determination and the method of computation of the data, the calculations for a typical experiment are given in table 2.

RESULTS

All of the results of the experiments are summarized in table 3. Along with each solution number are given symbols to indicate the method of preparation of that solution. In this code "i" means that the solution was made independently of all other solutions while, for example, "d2" indi-

cates that that solution was prepared by dilution of solution no. 2 of that series. With the exception of lithium bromide solution No. 5, each value of β is the mean of at least two independent measurements. In

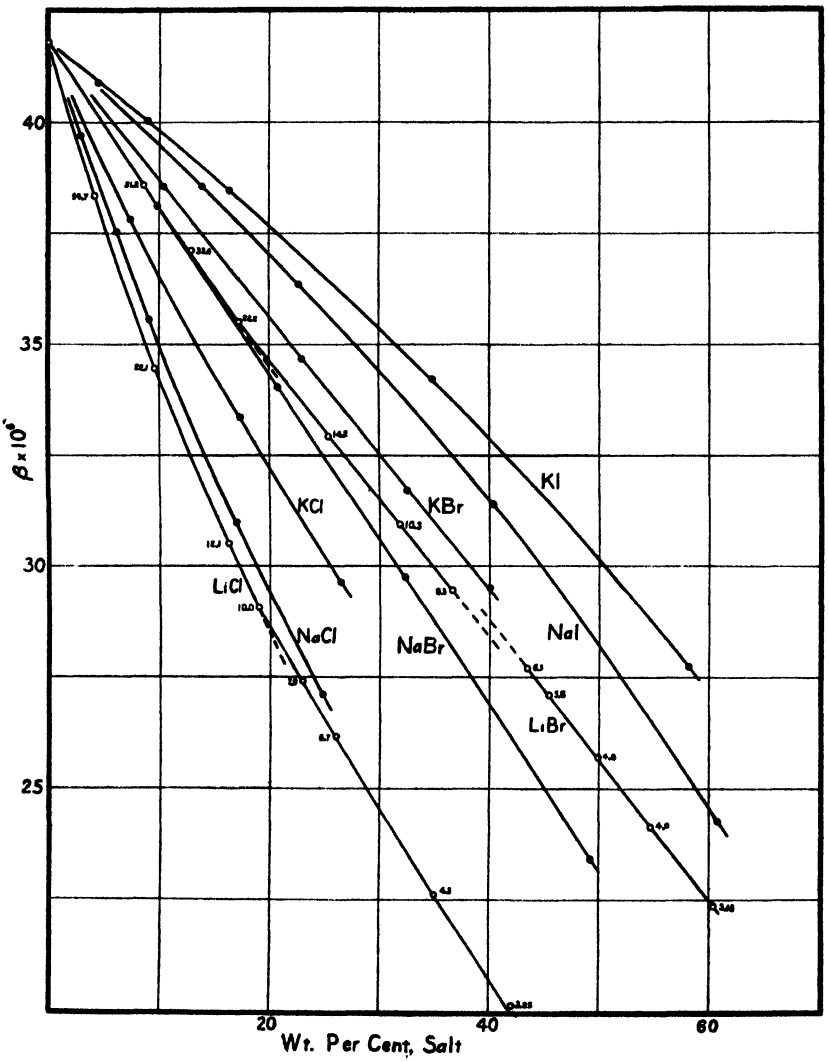

FIG. 1. THE COMPRESSIBILITY COEFFICIENTS OF SOLUTIONS PLOTTED AGAINST THE CONCENTRATION

order to have a rough measure of the uncertainty of the mean value of β there is given in the last column of table 3 the average deviation of the individual values of β from the given mean, expressed in the units of the compressibility coefficient. Attention is called to the fact that a number

of improvements in both technique and apparatus were made in the course of the compressibility measurements of solutions of potassium bromide and potassium iodide and of lithium chloride solution No. 1, which were the first to be investigated. For this reason the β values of these solutions are not so precise as those of the other solutions, as is evident from the data in the last column.

Figure 1 is presented to show the nature of the variation of the compressibility coefficient with the composition of the solutions. It can be seen that the anion determines both the relative position and the shape of the curves drawn through the plotted points. Thus, the lines representing the chlorides are all convex upwards; the lines representing the iodides are all convex downwards; and the lines representing the intermediate bromides have been drawn straight. The solutions of the two lithium salts, however, exhibit some noteworthy anomalies. Since these anomalies are apparently associated with the molecular composition of the solutions, the number (N) of moles of water per mole of salt for the various solutions is given in the graph alongside the plotted points. In the case of the lithium chloride solutions there is a definite break in the variation of β with concentration at the solution with the composition $N = 10$. This critical point is the same as that found from the examination of such other properties of lithium chloride solutions as the density and magnetic susceptibility. As a matter of fact the investigation (8) of this last-named property indicated that the magnetic susceptibility of lithium chloride has two definite values, one in solutions less concentrated than $N = 10$, and the other in solutions more concentrated than $N = 6$. The transition between these two distinct values takes place in the concentration region $10 > N > 6$. Whether this second change in the solution state would affect the compressibility of the solutions cannot be ascertained from the present data. The possibility of a second break in the β–concentration curve at a point where $N = 6$ is not entirely out of the question, because the plotted point $N = 3.25$ does not fall on the curve as drawn.

Lithium bromide solutions appear to be more irregular even than those of lithium chloride. In the first place the compressibility coefficients of these solutions do not follow the usual sequence Li–Na–K. In the second place there are two abrupt changes in the variation of β with concentration. One of these breaks occurs in rather dilute solutions, somewhere in the concentration region $30 > N > 24$. The change in the rate of variation of β with percentage composition at this point is not very different from that found in the lithium chloride solutions. The second break in concentrated solutions $8 > N > 6$ is of an entirely different type. The rate of change of β with concentration does not appear to be affected by the change in the solution state, but the β values in the more concentrated solutions are 0.4×10^{-6} units higher than they would be if there were no break in

the variation of β with concentration. Furthermore, this change in the solution state must take place in a rather short concentration range which we hope to explore more carefully. In conclusion it should be noted that Hüttig and Keller (5) found that the densities, refractive indices, and coefficients of extinction of the lithium halide solutions do show discontinuities with changes in concentration when $N = 6$, near 30, and 75.

Further discussion of these results from a different point of view will be the subject of another paper.

In conclusion we wish to express our gratitude to Professor Arthur B. Lamb of Harvard University for the loan of the piston of the pressure gage used in this investigation.

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THE MICRODETERMINATION OF VAPOR DENSITY

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In a recent research we had need of an apparatus for determining the vapor densities of a series of compounds which could be vaporized only under reduced pressure. Such determinations have been made in the past, but usually with a constant volume apparatus; the apparatus now described possesses features such as the simplicity of manipulation and the rapidity with which determinations are made which should commend it to anyone who is determining the vapor densities of substances which decompose on boiling at atmospheric pressures or substances available to the extent of only a few milligrams. The method is also useful for substances whose high boiling point renders the determination of their vapor density at ordinary pressures somewhat difficult.

The apparatus, shown in figure 1, consists of a vaporization tube, A, 1 meter in length and of 300-cc. capacity, closed with a well-fitting rubber bung and surrounded with a copper jacket, B. The latter is lagged with asbestos, fitted with a side-arm condenser, C, and is attached to the flask, D, in which the bath liquid is heated. The vaporization tube connects to two side tubes, one, on the left, containing a phial with a few milligrams of the substance under examination and a nail, which, when pulled by a magnet, ejects the phial into the vaporization tube. The other side tube leads to a manometer, E, containing a light liquid of low vapor pressure (ethyl phthalate or nitrobenzene), to one arm of a Hempel buret, F, containing clean, dry mercury, and to a tap, G, through which the apparatus was exhausted by means of a Cenco pump. The other arm of the Hempel buret was connected through a reservoir of 2-liters capacity, H, to stabilize the pressure to the tap, K, and thence to the common lead to the pump. Another tap, not shown in the diagram, enabled the pump to be cut off from the rest of the apparatus. All joints were sealed with Picein wax.

In practice it was found that, owing to minute traces of volatile material in the gauge liquid which could not be removed even by long heating *in vacuo*, the manometer, E, did not record absolute pressures. It was used, therefore, merely as a pressure indicator and a McLeod gauge, M, was incorporated in the system.

In making a determination the bath was heated until the liquid was re-

fluxing well up the condenser arm, and the apparatus was exhausted with all the taps open until a pressure of 5 to 10 mm. of mercury was registered

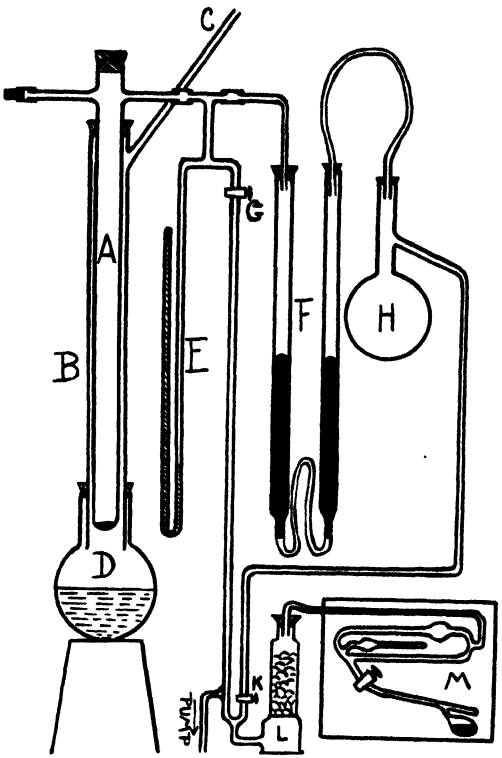

FIG. 1. APPARATUS FOR DETERMINATION OF VAPOR DENSITY UNDER REDUCED PRESSURE

TABLE 1

BATH LIQUID	TEMPERATURE	SUBSTANCE	QUANTITY USED	MOLECULAR WEIGHT (OBSD.)	MOLECULAR WEIGHT (CALCD.)
	degrees C.		*mg.*		
Nitrobenzene	211	Dibromobenzene	4	224	236
Nitrobenzene	211	Dibromobenzene	4	246	236
Nitrobenzene	211	Anthracene	5	182	178
Water	100	Acetoacetic ester	5	128	130
Xylene	143	Carvone	5	146	150
α-Pinene	156	Geranyl acetate	7	206	196
α-Pinene	156	Geranyl acetate	6	201	196

on the manometer, E, when the taps were closed. The phial was projected into the vaporization tube, its fall being broken by a small quantity of

fusible metal at the bottom of the tube (fusible metal is superior to glass wool, which is liable to evolve occluded gases under reduced pressure). Vaporization occurs in two minutes at the most, the gauge, E, being maintained at a constant level during the vaporization by lowering the right hand arm of the Hempel buret. When the vaporization was complete the taps G and K were opened, the gauge, E, restored to its original level by further slight evacuation, and the pressure recorded with the McLeod gauge. The calculation follows that of the ordinary Victor Meyer determination.

The method is superior to the constant volume method under reduced pressure since (1) it avoids the necessity for capillary tubing outside the heating jacket, and (2) it does not require a knowledge of the volume of the apparatus and the temperature of the jacket. One precaution must be mentioned. On admitting air at the conclusion of an experiment a film of moisture invariably condenses on the sides of the Hempel buret. This is revaporized during another experiment and causes a considerable error. It is necessary at the end of a determination to let the vacuum down with the mercury column fully raised and then to lower the column after re-evacuation and to warm the sides of the buret. The buret arms may be enclosed in water jackets at constant temperature.

Table 1 exemplifies some of the results obtained. The apparatus gives results correct to 3 to 5 per cent with ordinary precautions, an error which might easily be reduced to 1 to 2 per cent if so desired.

A DISCUSSION OF PATRICK AND ALLAN'S ARTICLE ON DIFFUSION OF ELECTROLYTES IN SILICA GEL

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In a recent article by Patrick and Allan (1), entitled "Diffusion of Electrolytes in Silica Gel," the authors in their discussion make the following statement: "According to the Nernst theory of diffusion, which leads to the elementary explanation of the liquid potential, a mobile ion should increase the rate of diffusion of a more slowly moving oppositely charged ion. Furthermore in the case of mixed electrolytes the more mobile ion will be retarded by the other ions, which in turn will experience an increase in mobility. This simple theory has been found to be in agreement with much experimental fact when dealing with ordinary diffusion phenomena. However, in the case of diffusion from a solution through a rigid gel structure, the above explanation no longer holds. Our washing of impregnated gels showed a marked retardation of the diffusion of the salt in the presence of acid, while our diffusion experiments through silica gel discs not only definitely proved the same point, but we were also able to show that the diffusion of the acid was speeded up in the presence of salt. These facts are in conflict with the Nernst theory; incidentally, Nernst never applied his ideas to systems such as used in this study."

The purpose of the present communication is to show that "these facts" are not only in qualitative, but also, in spite of the high concentrations of the electrolytes, in excellent quantitative agreement with Nernst's theory of diffusion of electrolytes.

In Patrick and Allan's diffusion experiments, one face of a cylinder of silica gel was in contact with a stirred aqueous solution of the electrolyte or electrolytes; the opposite face was bathed in a stream of pure water. After a steady state of diffusion had been reached, the authors measured the quantity of electrolyte which diffused through the gel in twenty-four hours. Assuming the concentration of electrolyte to fall off linearly in the silica gel, the authors were able to calculate the diffusion coefficient, knowing of course the cross-section and length of the cylinder of gel.

Consider a solution in which the concentrations (in moles per cm.^{3}) of sodium chloride and hydrogen chloride are C_1 and C_2, respectively. We assume the solutions to be so dilute that the osmotic pressures P_1, P_2, and

P_3 of sodium, hydrogen, and chloride ions are given by the equations $P_1 = C_1RT$, $P_2 = C_2RT$, $P_3 = CRT = (C_1 + C_2)RT$. Let u_1, u_2, and u_3 be respectively the velocities of the ions in centimeters per second when unit force (apart from the frictional force) acts on one mole of each kind of ion. On account of the differences in the numerical values of u_1, u_2, and u_3, the ions will be acted on by electric forces. We represent the potential of these forces by V expressed in such units that $-\frac{dV}{dX}$ is the electric force in the positive X-direction on one gram-equivalent of positive ions. It readily follows that the number of moles (S) diffusing per second through the constant cross-section q will be given for the three kinds of ions by the equations:

$$S_1 = -qu_1\left(\frac{dP_1}{dX} + C_1\frac{dV}{dX}\right) \text{ for } Na^+ \text{ ions}$$

$$S_2 = -qu_2\left(\frac{dP_2}{dX} + C_2\frac{dV}{dX}\right) \text{ for } H^+ \text{ ions}$$

$$S_3 = -qu_3\left(\frac{dP_3}{dX} - C_3\frac{dV}{dX}\right) \text{ for } Cl^- \text{ ions}$$

By means of the condition, $S_1 + S_2 = S_3$, we can eliminate $\frac{dV}{dX}$ from these equations. On account of the linear fall in C_1 and C_2 through the gel, the ratio $\frac{C_2}{C_1} = r$ is constant throughout the cylinder and $\frac{dC_2}{dX} = r\frac{dC_1}{dX}$. Substituting for P_1 and P_2 the expressions C_1RT and C_2RT, respectively, we find

$$S_1 = -q\frac{2u_1u_3}{u_1 + u_3}RT\frac{dC_1}{dX}\left[\frac{1 + r}{1 + \left(\frac{u_2 + u_3}{u_1 + u_3}\right)r}\right] \tag{1}$$

$$S_2 = -q\frac{2u_2u_3}{u_2 + u_3}RT\frac{dC_2}{dX}\left[\frac{r + 1}{r + \left(\frac{u_1 + u_3}{u_2 + u_3}\right)}\right] \tag{2}$$

Representing by D_{10} the diffusion coefficient of sodium chloride in the absence of hydrogen chloride, and by D_1 the diffusion coefficient when the ratio of hydrogen chloride to sodium chloride is r, we find from equation 1

$$D_1 = D_{10}\left[\frac{1 + r}{1 + \left(\frac{u_2 + u_3}{u_1 + u_3}\right)r}\right] \tag{3}$$

Similarly if D_{20} and D_2 are the diffusion coefficients of hydrogen chloride in the absence and in the presence of sodium chloride, respectively, we find from equation 2

$$D_2 = D_{20}\left[\frac{r+1}{r+\left(\frac{u_1+u_3}{u_2+u_3}\right)}\right] \tag{4}$$

Since u_1 (for Na^+) is less than u_2 (for H^+), it follows from equations 3 and 4 that

$$D_1 < D_{10} \tag{5}$$

$$D_2 > D_{20} \tag{6}$$

The expressions 5 and 6 are in qualitative agreement with the experimental results obtained by Patrick and Allan. Quantitatively we have

$$\frac{D_1}{D_{10}} = \frac{1+r}{1+\left(\frac{u_2+u_3}{u_1+u_3}\right)r} \tag{7}$$

$$\frac{D_2}{D_{20}} = \frac{r+1}{r+\left(\frac{u_1+u_3}{u_2+u_3}\right)} \tag{8}$$

We can test equations 7 and 8 by replacing u_1, u_2, and u_3 by the equivalent ionic conductances U_1, U_2, U_3. Some error will be introduced by taking for the equivalent ionic conductances their values at infinite dilution. From the values at 18°C. we find, using the appropriate temperature coefficients, the following equivalent ionic conductances at 32.5°C.; $Li^+ = 45.7$, $Na^+ = 58.5$, $K^+ = 84.5$, $H^+ = 387.0$, and $Cl^- = 85.8$. We give in tables 1 and 2 the values of $\frac{D_1}{D_{10}}$ and $\frac{D_2}{D_{20}}$ obtained experimentally by Patrick and Allan and those calculated by equations 7 and 8.

ABSOLUTE VALUES OF THE DIFFUSION COEFFICIENTS

The absolute value of the diffusion coefficient in water of a single electrolyte (e.g., sodium chloride) is given according to Nernst by the equation

$$D_{\text{calcd.}} = \frac{2u_1u_3}{u_1+u_3}RT$$

$$= \frac{0.04485}{86400} \times \frac{273+t}{273+18}\frac{U_1U_3}{U_1+U_3} \text{ cm.}^2 \text{ per second}$$

For the diffusion through silica gel, Patrick and Allan obtained the diffusion coefficient from the equation

$$S_1 = qD\frac{dC_1}{dX}$$

where S_1 is the number of moles (e.g., of sodium chloride) diffusing per second and q is the cross-section of the gel. We give in table 3 the values

TABLE 1

Observed and calculated values of the relative diffusion coefficient

Salt, 0.90 N; HCl, 1.15 N; r = 1.28; t = 32.5°C.

SALT	$\frac{D_1}{D_{10}}$		$\frac{D_2}{D_{20}}$	
	Observed	Calculated	Observed	Calculated
LiCl	0.41	0.41	1.43	1.46
NaCl	0.41	0.44	1.50	1.44
KCl	0.44	0.50	1.45	1.39

TABLE 2

Observed and calculated values of the relative diffusion coefficient

Salt, 1.80 N; HCl, 1.15 N; r = 0.64; t = 32.5°C.

SALT	$\frac{D_2}{D_{20}}$	
	Observed	Calculated
LiCl	1.79	1.78
NaCl	1.91	1.73
KCl	1.80	1.64

TABLE 3

Observed and calculated values of the diffusion coefficient

SALT	ORIGINAL CONCENTRATION	D_{obsd}	D_{calcd}	$\frac{D_{calcd}}{D_{obsd}}$
LiCl	0.90	1.92×10^{-6}	1.62×10^{-5}	8.4
NaCl	0.90	3.43×10^{-6}	1.90×10^{-5}	5.5
KCl	0.90	4.69×10^{-6}	2.32×10^{-5}	5.0
HCl	1.15	8.52×10^{-6}	3.83×10^{-5}	4.5

of $D_{obsd.}$ (obtained by Patrick and Allan) and the values of $D_{calcd.}$ (calculated on the Nernst theory for diffusion in water).

A possible explanation of the values given in the last column of table 3 can be furnished by supposing that the water in the gel through which the

ions diffuse occupies a fairly definite fraction of the apparent volume of the gel. In other words, as a diffusion medium the cylinder of gel is equivalent to a cylinder of water of the same length but of much smaller cross-section,—about one-fifth to judge from the experiments with sodium chloride, potassium chloride, and hydrogen chloride, and about one-eighth when lithium chloride is used. The differences among the values of the last column of table 3 are too large to be attributed to experimental errors only; our picture of the state of a salt solution present in the gel is probably too much simplified.

In conclusion, I think it can be said that the diffusion of electrolytes in silica gel seems to take place in essentially the same way as in water and that in both cases the Nernst theory of diffusion of electrolytes is quantitatively applicable.

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THE APPARENT VOLUMES OF SALTS IN SOLUTION AND THEIR COMPRESSIBILITIES

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In recent years there has been a marked revival of interest in the problem of the volume changes that occur when a solution undergoes a change in concentration. An important factor in this was the discovery by Masson (11), and independently by Geffcken (4), of a simple relationship between the apparent molal volume of the solute and the concentration of the solution. As an outgrowth of previous studies (16, 17) of this empirical rule of Masson, the question of the effect of pressure on the apparent volumes appeared to be of considerable interest and significance. This question is the subject of the present paper. Because the existing compressibility data were considered to be too fragmentary for a satisfactory treatment of this problem, systematic measurements of the compressibility coefficients of solutions of the alkali halides were undertaken. The results of the first series of these experiments have already been reported (20) and will be used exclusively in this study.

The apparent molal volume (ϕ) of a solute is defined as

$$\phi = V - n_1 V_1 \tag{1}$$

where V is the volume of solution containing 1 gram-mole of solute, V_1 is the volume of 1 gram-mole of pure water at the temperature of the solution, and n_1 is the number of moles of water present in the solution. The compressibility of the apparent molal volume, which will be designated as $\bar{B}$ and which may be termed the apparent molal compressibility of the solute, is defined by the expression:

$$\bar{B} = -\frac{\partial \phi}{\partial P} = V\beta - n_1 V_1 \beta_1 \tag{2}$$

where $\beta \left[= -\frac{1}{V}\frac{\partial V}{\partial P} \right]$ is the compressibility coefficient of the solution and β_1 is that of water.

Masson's empirical rule for strong electrolytes may be expressed as follows:

$$\phi = kc^{\frac{1}{2}} + \phi^0 \tag{3}$$

Here k and ϕ^0 are constants characteristic of each electrolyte and temperature, and c is the concentration expressed in moles per liter. Since this equation[1] is the basis of the present inductive study, a brief review of its status will not be out of place. The applicability of this relationship was tested originally by Masson for a number of salts of diverse valence types. Subsequent more systematic tests (5, 15, 16) have covered the salts of the alkali halides and the alkaline earth halides. In general, these tests have all tended to confirm the validity of the empirical rule with the following qualifications. Equation 3 does not hold in extremely concentrated solutions of certain salts, such as the lithium halides, where chemical hydration is supposed to be a disturbing factor. Further, the above-named tests have been limited in scope to solutions more concentrated than 1 molar. In solutions less concentrated than this the ϕ values are too uncertain, because of the tremendous magnification of the experimental error involved in their calculation, to permit of a conclusive test. Within the past year, however, Geffcken (6, 7) and his coworkers have improved the technique for making the extremely precise density measurements which are essential for the calculation of accurate values of ϕ in very dilute solutions. Although not all of their measurements have been published, the results that are available may be summarized briefly as follows. With solutions of sodium bromide and ammonium nitrate at 25°C., equation 3 appears to be valid over the concentration ranges, 0.02 M to 5.5 M and 0.05 M to 7.5 M, respectively. In the case of sodium chloride solutions a break in the $\phi - c^{\frac{1}{2}}$ plot occurs at about 0.4 M. Solutions of sodium carbonate, although apparently normal at high concentrations, are quite irregular in concentrations less than 0.1 M. The abnormality consists not only in a deviation from Masson's rule, but in the most extreme dilutions the apparent molal volume begins to increase with decreasing concentration. These various tests may be summarized by stating that there is no reason to question the applicability of equation 3 to concentrated solutions of strong electrolytes, but that an uncertainty still exists regarding its general validity in dilute solutions. In this connection it may be mentioned also that Redlich and Rösenfeld (13) have given a derivation of equation 3 based on the Debye-Hückel theory and thermodynamics according to which the constant k has the same value for all electrolytes of the same valence type. In order to reconcile the actual data with their theoretical equations, they conclude that the latter hold only in very dilute solutions and that in concentrated solution the variation of ϕ with $c^{\frac{1}{2}}$ is not linear. Since some nonelectrolytes also agree with Masson's rule, the significance of conclusions based upon the Debye-Hückel theory is open to question (9) because such

[1] A review of this equation and of the similar expressions for the apparent heat capacity and apparent compressibility has been published recently by Gucker (9).

substances would not have the ion atmosphere which is a basic postulate of the theory.

From Masson's equation a relationship between the apparent molal compressibility $\bar{B}$ and concentration can be derived directly. If we differentiate equation 3 with respect to pressure, we get

$$\frac{\partial \phi}{\partial P} = \frac{\partial k}{\partial P} c^{\frac{1}{2}} + k \frac{\partial c^{\frac{1}{2}}}{\partial P} + \frac{\partial \phi^0}{\partial P} \tag{4a}$$

Since $c = 1000/V$, it follows that

$$\frac{\partial c^{\frac{1}{2}}}{\partial P} = -\frac{1}{2} \frac{c^{\frac{1}{2}}}{V} \frac{\partial V}{\partial P} = \frac{1}{2} \beta c^{\frac{1}{2}} \tag{4b}$$

where β is the compressibility coefficient of the solution. Now, if we let $f = \frac{1}{2} k \beta c^{\frac{1}{2}}$ and if, in accordance with equation 2, we designate $-\frac{\partial \phi}{\partial P}$ and $-\frac{\partial \phi^0}{\partial P}$ by $\bar{B}$ and $\bar{B}^0$, respectively, equation 4a can be written as:

$$\bar{B} + f = -\frac{\partial k}{\partial P} c^{\frac{1}{2}} + B^0 \tag{5}$$

This equation will form the basis of much of our subsequent discussion. It can be tested most conveniently in the form written, as a linear relationship between $(\bar{B} + f)$ and $c^{\frac{1}{2}}$, which quantities can be calculated from experimental data. A plot of these variables will be presented later and from it the terms $-\frac{\partial k}{\partial P}$ and $\bar{B}^0$ can be derived directly.

Since our measurements designed to test equation 5 were initiated, relationships involving $\bar{B}$ or closely related factors have been proposed by two investigators. Adams (1), from his compressibility measurements of several sodium chloride solutions over a wide pressure range, calculated the fictive or partial compressibility of the solution which, for an infinitely dilute solution, is the same as the apparent compressibility. In a later paper Adams (2) stated that the specific apparent compressibility of the same solute could be represented by a linear function of the square root of the mole or mass ratio. Such a function implies that Masson's relation holds also "if the mole ratio or mass ratio is substituted for the volume concentration." A study of the properties of the apparent molal compressibility of solutes in solution has been published recently by Gucker (10), who recalculated for this purpose most of the available data. His conclusion was that $\bar{B}$ is a "linear function of $c^{\frac{1}{2}}$ over a wide range of concentration, temperature, and pressure." In a subsequent article (9) he showed that this relationship could be derived from the Debye-Hückel theory of solu-

TABLE 1

Values of the various solution factors at 35°C.

c	c_{200}	ϕ	ϕ_{200}	$-\bar{B}$	f
		Lithium chloride solutions			
0.9895	0.9971	18.60	19.06	27.09	0.21
2.3900	2.4065	19.30	19.75	22.69	0.29
4.1767	4.2024	20.08	20.45	18.62	0.34
4.9401	4.9690	20.22	20.57	17.34	
6.1272	6.1609	20.50	20.79	14.91	
7 0479	7.0849	20.62	20.89	13.90	
8.0654		20.74			
9.9576	10.0028	20.86	21.07	10.55	
12.5274	12.5780	21.00	21.17	8.83	
		Lithium bromide solutions			
1.0486	1.0568	25.61	26.01	20 00	0.14
1.6322	1.6444	25.80	26 15	17.58	0.16
2.2444	2.2605	26.01	26 35	17 20	0 18
3.5318	3.5552	26.36	26.64	14.13	0.22
4 6927	4.7219	26 54	26.78	12.05	0 23
5.6371	5 6705	26.67	26 88	10.74	0.24
7.1335	7 1732	26 62	26 79	8 62	0 25
7.6009	7 6423	26 64	26 80	8 07	
8.7621	8.8074	26 58	26.73	7 27	
10.1416	10.1908	26 42	26 55	6 38	
11.9692	12.0230	26 29	26 39	5 25	
		Sodium chloride solutions			
0.4971	0.5011	18.71	19.39	34.22	0.21
1.0872	1 0954	19.33	19 95	31.10	0.29
1.6571	1.6690	19 67	20.26	29.44	0.34
3 2457	3.2659	20 73	21.22	24 65	0.41
5.0080	5.0353	21 57	21 98	20.34	0.44
		Sodium bromide solutions			
1.0256	1.0335	26 19	26.69	25 10	0.27
2 3703	2.3865	26.88	27.28	21.50	0.28
4.0994	4.1240	27.73	28.09	17 80	0.33
7.3957	7.4305	28,72	28.98	12.84	0.34
		Sodium iodide solutions			
1 0287	1.0368	37.47	37.79	15.93	0.17
1.8141	1.8274	37.97	38.25	14.14	0.21
3 8322	3 8565	38.56	38.78	11.04	0.26
7.3258	7.3615	39.27	39.42	7.50	0.28

TABLE 1—(*Concluded*)

c	c_{200}	ϕ	ϕ_{200}	$-\bar{B}$	f
Potassium chloride solutions					
1 0397	1 0476	29.40	29 92	25 90	0.36
2 5671	2 5758	30 65	31 05	20 11	0.50
4 1769	4 2018	31.62	31 94	15 90	0 52
Potassium bromide solutions					
0.4591	0 4628	35.87	36 43	27 70	0.21
0 9416	0 9489	36.35	36.74	19 43	0.29
2 2806	2 2964	37 32	37.63	15.62	0 41
3 4987	3 5210	38.02	38 28	12.92	0 46
4 5951	4 6224	38 47	38 68	10.67	0.49
Potassium iodide solutions					
0 2728	0 2750	47 47	47 76	14.29	0 13
0.5732	0 5779	47.34	47.56	10 92	0 19
1 1131	1.1217	47.93	48.13	10 15	0 25
2 7763	2.7954	48 65	48 79	6 96	0.36
5.9006	5 9335	49 80	49 86	3 00	0 42

tion in conjunction with certain thermodynamic relationships. The only difference between Gucker's equation and our equation 5 is the factor f. The magnitude of this factor and its variation with concentration are such that it would be futile to attempt to prove one equation to be more nearly correct than the other without more precise compressibility data than those obtainable at present. We shall therefore make no attempt to compare the two expressions in this paper. Nevertheless, since both equations are empirical, there would seem to be an advantage in choosing to work with the one (equation 5) which is mathematically consistent with the fairly well established empirical rule of Masson. Furthermore, the term $(\bar{B} + f)$ may be regarded as a simpler concept than the calculated quantity $\bar{B}$, which involves concentration as a dependent variable. Application of pressure to a solution produces an increase in concentration which, in turn, would result normally in an increase in ϕ. This small increase in ϕ is one of the pressure effects included in the quantity $\bar{B}$. Since, however, it is equal to

$$f = k \frac{\partial c^{\frac{1}{2}}}{\partial P} = \frac{\Delta\phi}{\Delta P}$$

when k, ϕ^0 are constant, the term $(\bar{B} + f)$ represents the change in ϕ with pressure when the concentration is considered an independent variable.

Before describing the calculations of the various quantities which we

shall require in our test of equation 5, there is a question of procedure that should first be pointed out. Since these quantities are all functions of pressure it is obviously desirable that they refer to the solution system under the same pressure. This condition cannot be fulfilled exactly by the use of our data because the compressibility coefficient measured is for a system under a pressure of 200 metric atmospheres, whereas the density data are for solutions under only atmospheric pressure. The error introduced by this discrepancy can be reduced to a negligible magnitude if all the quantities are calculated to apply to a system under the higher pressure, a fact which will be evident from the following description of the calculations of the quantities in question.

All the factors which we shall need in this study are assembled in table 1 and were calculated from the data for solutions at 35°C., given in the article already referred to. Certain symbols which will be employed may be defined at the outset:

$\%$ = percentage by weight of solute in solution.

M = gram-molecular weight of solute.

d, d_1 = densities of solution and pure water.

β, β_1 = average compressibility coefficients of solution and water at 200 megabars (or metric atmospheres) pressure. For the sake of brevity we shall refer hereafter to the pressure units simply as "atmospheres."

c = concentration in gram-moles of solute per liter of solution.

$$c = \frac{\% \cdot d}{M} \cdot 10$$

The precision of the calculated values of c is better than 0.02 parts per thousand. Values of c are given in the first column of table 1.

c_{200} = concentration of the solution under a pressure of 200 megabars. This quantity was also calculated by means of the above formula, using the density of the solution at 200 atmospheres. This density was computed by taking

$$d_{200} = d(1 + 200\beta)$$

This correction is, to be sure, only a first approximation, because the compressibility coefficient used does not give the change in volume over the pressure range 0 to 200 but gives the rate of change when the system is under a pressure of 200 metric atmospheres. A further correction to take this fact into account would be of the second order and would be negligible. Values of c_{200} are given in the second column of table 1.

ϕ = the apparent molal volume at atmospheric pressure expressed in cubic centimeters.

$$\phi = \frac{M}{\%d \cdot 10} - \frac{(100 - \%) \cdot M \cdot 1000}{\%d_1}$$

Since ϕ is a difference between two terms, its precision is very much less than that of the experimentally determined quantities and decreases rapidly with decreasing concentration. While in concentrated solutions the uncertainty is about 0.02 cc., in a 1 molal solution it may be 0.1 cc. or even slightly greater. Values of ϕ are given in the third column of table 1.

ϕ_{200} = the apparent molal volume at 200 atmospheres pressure, expressed in cubic centimeters. The calculation of these quantities is the same as that just described with the difference that the densities were corrected to the higher pressure by the formula given in the paragraph under c_{200}. In practice this density correction is most conveniently accomplished by subtracting 200 $\times$ $\bar{B}$ (see next paragraph) from the corresponding ϕ values. The error introduced by this approximation into the calculated values of ϕ_{200} is less than the uncertainties of the ϕ values. Values of ϕ_{200} are given in the fourth column of table 1.

$\bar{B}$ = apparent molal compressibility at 200 atmospheres pressure expressed in cc. atm.$^{-1}$ $\times$ 10^4.

$$B = \frac{M\beta}{\%d \cdot 10} - \frac{(100 - \%)M \cdot \beta_1 \cdot 1000}{\%d_1}$$

Attention is called to the fact that no correction for the change in density with pressure has been made, as was necessary in the calculation of the ϕ_{200} values. The reason for this is that the compressibility actually measured is not the ideal coefficient but the average coefficient over the pressure range 100 to 300 metric atmospheres and is calculated from the following measured quantities:

$$\beta = -\frac{1}{V_0}\frac{\Delta V}{200}$$

Here ΔV refers to 200 atmospheres, but the V_0 is the volume at 1 atmosphere pressure. While the value of this last term at 200 atmospheres pressure could be computed approximately, the correction applied would be cancelled by the

correction that would then have to be applied to d_δ and d_1 in calculating $\bar{B}$. In short, by not correcting either V_0 or the densities we get $\bar{B}$ at 200 megabars pressure without any qualification. Since we shall not be able to use values of $\bar{B}$ at atmospheric pressure, we shall omit a designative subscript. With regard to the precision of these computed $\bar{B}$ values only the general statement can be made that they are the least precise quantities which we shall employ. As in the case of the apparent molal volumes, the uncertainty in $\bar{B}$ increases with decreasing concentration. Using sodium chloride solutions as an example, the uncertainty in the $\bar{B}$ value of the most concentrated solution is probably only two units in the second decimal, whereas in the 1 molal solution the uncertainty may amount to at least one unit in the first decimal. Values of $\bar{B}$ are given in the fifth column of table 1.

f = correction factor already defined (equation 5) as $\frac{1}{2}\beta k c^{\frac{1}{2}}$ and is expressed in the same units as $\bar{B}$. Both the $c^{\frac{1}{2}}$ and the k values used in these calculations were for systems under a pressure of 200 atmospheres. The k values used are given in table 2. Values of f are given in the sixth column of table 1.

In view of the fact that the values of $\bar{B}$ are known only for systems under 200 atmospheres pressure and that therefore our examination of equation 5 is limited to such systems, we are obliged to consider first the question of the validity of Masson's equation for systems under pressure. As a preliminary basis for the consideration of this question ϕ and ϕ_{200} have been plotted (figure 1) against $c^{\frac{1}{2}}$ and $c^{\frac{1}{2}}_{200}$, respectively. The values of the Masson constants as found from the drawn lines in the graph are given in table 2.

Concerning the ϕ, $-$ $c^{\frac{1}{2}}$ plots for systems under atmospheric pressure, only a few observations are needed. The deviations of the plotted points from the drawn straight lines are less than the estimated uncertainties of the plotted quantities. The Masson constants for some of the solutions under consideration have also been determined by Geffcken (5) and, for the sake of comparison, are given in parentheses in table 2. There is excellent agreement between the two sets of constants except in the case of the potassium bromide solutions. The deviation from the linear relationship which is very evident in the concentrated solutions of the two lithium salts has been noted previously at other temperatures. The concentration at which the linear relationship breaks down is a matter of some interest. Masson's conclusion that the limit with lithium chloride solutions is a solution with the composition $LiCl + 10H_2O$ is confirmed by our data ($c^{\frac{1}{2}}$ =

2.04). The limit for the lithium bromide solutions cannot be established so clearly. The limiting solution of this salt contains 24 to 30 moles of water per mole of salt. In the more concentrated solutions of these lithium salts ϕ appears to be a linear function of the number of moles of water present. This question we intend to treat in a separate note.

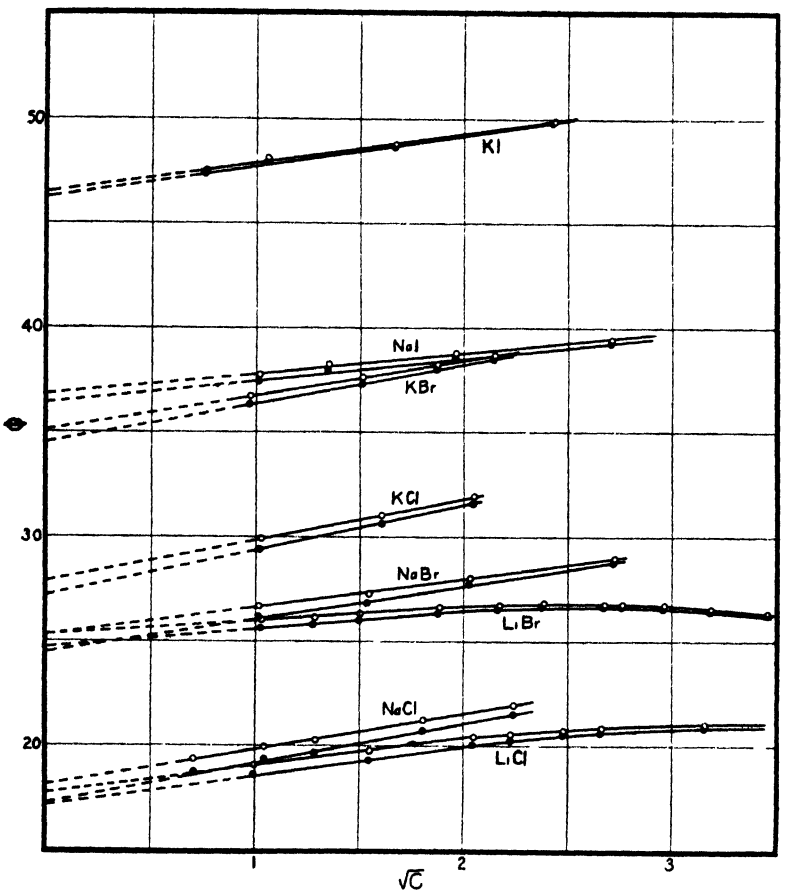

FIG. 1. APPARENT MOLAL VOLUMES PLOTTED AGAINST THE SQUARE ROOT OF THE CONCENTRATION WHEN THE SOLUTIONS ARE UNDER ATMOSPHERIC PRESSURE (OPEN CIRCLES) AND UNDER A PRESSURE OF TWO HUNDRED METRIC ATMOSPHERES (SOLID DOTS)

We shall look upon the $\phi - c^{\frac{1}{2}}$ plots for solutions under pressure as a means of testing Masson's empirical equation for solutions under conditions entirely different from those for which the equation has previously been shown to hold. So far as can be judged from an inspection of the graph, the linear relationship holds as well for solutions under pressure as for solu-

tions at atmospheric pressure. Further evidence supporting this tentative conclusion will be presented in the discussion of the next figure. We shall have occasion to use the constants (table 2) of the drawn lines later. The value of k_{200} has already been employed in computing the factor f (table 1). Attention should perhaps be called to the fact that increase in pressure results in an increase in ϕ^0 and a decrease in k. The only check on the present figures is with the ϕ values of sodium chloride solutions. The difference between ϕ_{200} and ϕ here is essentially the same as that (0.85 cc.) found by Adams (1) for the corresponding change in the partial molal volumes of

TABLE 2

Values of constants obtained from figure 1

SALT	ϕ^0	ϕ^0_{200}	k	k_{200}
LiCl	17 10	17.80	1 45	1.25
LiBr	24 75	25.35	0.75	0.65
NaCl	17.25 (17.25)	18.15	1 90 (1 92)	1.70
NaBr	24.45 (24.45)	25 31	1.55 (1.55)	1 34
NaI	36.45	36.85	1.08	0.97
KCl	27 22 (27 22)	27.90	2.13 (2.2)	2.00
KBr	34 55 (34 27)	35.15	1.85 (1 90)	1.65
KI	46.25 (46 25)	46 50	1 45 (1.42)	1.40

this salt, which in infinite dilution become identical with the apparent molal volumes.

In concluding our discussion of figure 1 it may be noted that the drawn lines are extended only to the concentration of the saturated solutions. For solutions at atmospheric pressure the necessary data were obtained from the measurements of Scott and Durham (18). The limits of the lines for solutions under pressure were determined by plotting the estimated value of ϕ_{200}, which was computed by the method already described from the ϕ value of the saturated solution at atmospheric pressure as read from the graph. In this procedure no allowance is made for the change in

solubility of the salt with pressure, which would be negligible for the small change in pressure involved.

In figure 2, values of $(\bar{B} + f) \times 10^4$ are shown plotted against values of $c^{\frac{1}{2}}_{200}$. From the fact that the plotted points fall so closely on the drawn

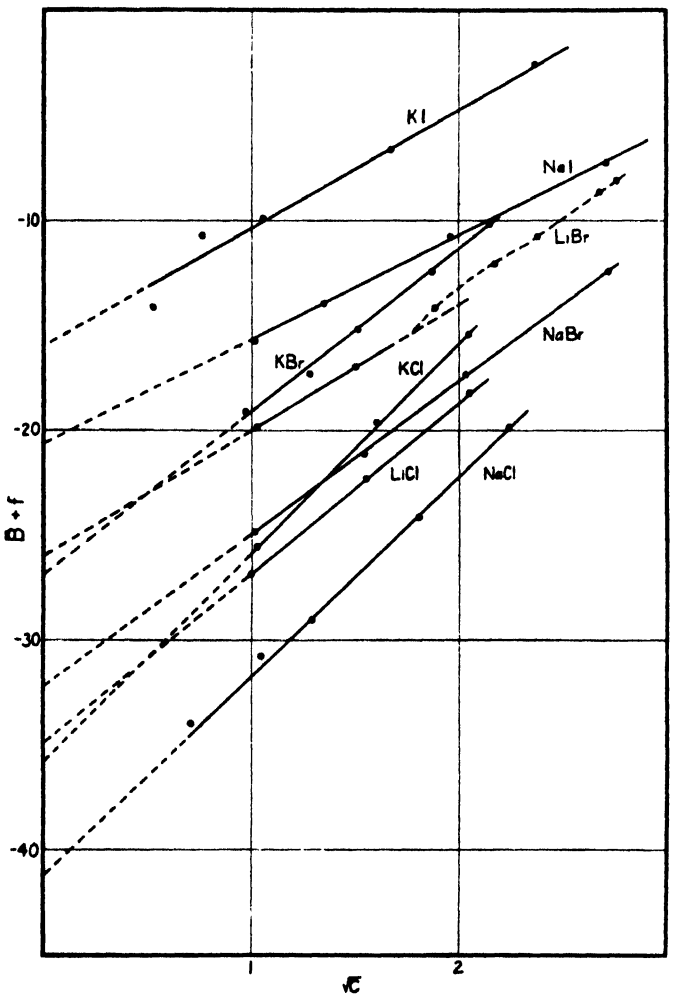

FIG. 2. PLOT SHOWING THE LINEAR RELATIONSHIP BETWEEN THE APPARENT COMPRESSIBILITY FACTOR $(\bar{B} + f)$ AND THE SQUARE ROOT OF THE CONCENTRATION

straight lines it may be concluded reasonably that the relationship between $(\bar{B} + f)$ and $c^{\frac{1}{2}}$ is linear within the limits of error of the quantities involved. Since this conclusion is in agreement with equation 5, which was derived from Masson's equation, we have here additional evidence of the appli-

cability of this empirical rule to solution systems under pressure. As a matter of fact, since this method of testing the basic equation is a great deal more sensitive to error than the $\phi - c^{\frac{1}{2}}$ plot, its outcome is especially valuable because it answers, so far as is possible at this time, the question of the validity of Masson's equation for systems under pressure.

The drawn lines have been extrapolated to values of $c = 0$. The corresponding values of $\bar{B}^0$ are given in table 3. These $\bar{B}^0$ values presumably represent simply the apparent compressibilities of individual ions, and consequently they might be expected to be the sum of the values characteristic of the component ions. That they are practically additive can be

TABLE 3

Data bearing on the constants of equation 5

SALT	$-\bar{B}^0 \times 10^4$	$\frac{-dk}{dP} \times 10^4$	$\frac{-d(\ln k_{200})}{dP} \times 10^4$	$\frac{-d(\ln k_{200})}{dP} \times 10^4$ CALCULATED
NaCl	41 20	9 50	5.58	5.71
NaBr	32 20	7 30	5 45	5 37
NaI	20.60	4 95	5 11	4 53
KCl	35 80	10 00	5 00	5 12
KBr	26 90	7.75	4 70	4 69
KI	16.00	5 65	4 03	3 94
LiCl	34 90	8 05	6 43	(6 07)
LiBr	26 00	5 99	9 22	(5 69)

TABLE 4

The differences between various combinations

M	$\bar{B}^0_{MCl} - \bar{B}^0_{MBr}$	$\bar{B}^0_{MBr} - \bar{B}^0_{MI}$	X	$\bar{B}^0_{NaX} - \bar{B}^0_{LiX}$	$\bar{B}^0_{KX} - \bar{B}^0_{NaX}$
Li	(8 9)		Cl	6 3	5.4
Na	9 0	11.6	Br	(6 2)	5.3
K	8 9	10.9	I		4 6

seen from the summary in table 4 of the differences between various combinations. The differences involving $\bar{B}^0$ of potassium iodide deviate slightly from the other corresponding differences; this is probably due to the greater uncertainty of the data of these solutions.

With the exception of the two lithium salts the upper limit of the drawn lines is the concentration corresponding to the saturated state as found in figure 1. The upper limit of the lines representing the solutions of lithium salts is the assumed limit of the applicability of Masson's equation. In the case of the lithium bromide solutions, the dotted line represents the variation of $\bar{B}$ with $c^{\frac{1}{2}}$ over the concentration region where f might be taken as zero since k (figure 1) is here approximately zero.

The slopes of the drawn lines are given in column 3 of table 3 and according to equation 5 are equal to $-\frac{\partial k}{\partial P}$ at 200 atmospheres pressure. The values of this constant are very nearly the same for sodium and potassium salts with a common anion, a fact which suggests that the effect of pressure on k is determined largely by the nature of the anion. The ratio $(-\frac{\partial k}{\partial P}/k)_{200}$ is equal to $-\frac{\partial \ln k_{200}}{\partial P}$ and is also given in table 2.

A rough check of the values of $\bar{B}^0$ and $-\frac{\partial k_{200}}{\partial P}$ can be found in an examination of the Masson constants given in table 2. If $\bar{B}^0$ is taken to be the average decrease in ϕ over the pressure range, 1 to 200 atmospheres, then $200\bar{B}^0$ should give approximately the difference $\phi^0 - \phi^0_{200}$. Similarly, the approximate difference $k - k_{200}$ can be calculated from the values of $\frac{\partial k_{200}}{\partial P}$. The average difference between $\phi^0 - \phi^0_{200}$ and $200\bar{B}^0$ is only 0.07 cc., and the average difference between $k - k_{200}$ and $200\frac{\partial k}{\partial P}$ amounts to a little less than 0.04 unit.

Before we take up the interpretation of the various properties of solutions which we have been able to derive from our data, it is desirable to consider first the derivation of an expression giving the compressibility coefficient of solutions, β, as a function of concentration. According to equations 1 and 3 we can write

$$\phi = V - n_1V_1 = kc^{\frac{1}{2}} + \phi^0$$

The differentiation of this equation with respect to pressure yields an expression which reduces to

$$\frac{\partial \phi}{\partial P} = -V\beta + n_1V_1\beta_1 = \left(\frac{\partial k}{\partial P} + \frac{k}{2}\beta\right)c^{\frac{1}{2}} - \bar{B}^0$$

Now, substituting $(V - \phi)$ for n_1V_1, $\frac{1000}{c}$ for V, and $kc^{\frac{1}{2}} + \phi^0$ for ϕ, we get:

$$\left(\frac{1000}{c} + \frac{k}{2}c^{\frac{1}{2}}\right)\beta = -\frac{\partial k}{\partial P}c^{\frac{1}{2}} + \left[\frac{1000}{c} - (kc^{\frac{1}{2}} + \phi^0)\right]\beta_1 + \bar{B}^0$$

which finally takes the form

$$\beta = \frac{1}{1 + \frac{k}{2000}c^{\frac{1}{2}}}[\beta_1 + Ac - Dc^{\frac{3}{2}}] \tag{6}$$

where the constant A is

$$\left(\frac{\bar{B}^0 - \beta_1\phi}{1000}\right)$$

and D is

$$\left(\frac{\frac{\partial k}{\partial P} + k\beta_1}{1000}\right)$$

Attention should be called to the fact that this expression for β as a function of concentration depends only on Masson's equation. Since it includes all the constants which we have obtained from the plots shown in figures 1 and 2, a good check on the consistency of our operations would be afforded by a comparison of the calculated and observed values of β. The necessary calculations have been carried out and the average absolute differences between calculated and observed β values are listed below:

Salt..	NaCl	NaBr	NaI	KCl	KBr	KI
Number of solutions.	5	4	4	3	4	5
Average difference	0 07	0.03	0.05	0.07	0 06	0.06

The magnitude of these differences is only slightly greater than the estimated uncertainties of the compressibility measurements. It should be noted, however, that in practically all cases the calculated β values were smaller than the observed ones. This difficulty arises from the fact that β is not the ideal coefficient and that the calculation of c_{200} is an approximation. To illustrate the sensitiveness of equation 6 to the last-named factor, it may be mentioned that an average increase of 0.05 unit in $\frac{\partial k}{\partial P}$ would completely remove the apparent defect in the calculated β values.

From the combination of his $\bar{B} - c^{\frac{1}{2}}$ and Masson's equation, Gucker (10) derived an expression which is the same as equation 6 with the denominator term missing. His derivation may be questioned on the ground that his apparent compressibility function is not mathematically consistent with Masson's equation.

The consideration of the significance of the apparent volume and the apparent compressibility is most conveniently approached from the standpoint of the relationship that exists between them. This relationship is gotten directly by eliminating the $c^{\frac{1}{2}}$ term from equations 3 and 5 and is

$$(\bar{B} + f)_c = \left(\frac{\partial \ln k}{\partial P}\right)\phi_c + \text{const.}$$

The subscript c is used to indicate that the two variables refer to the same

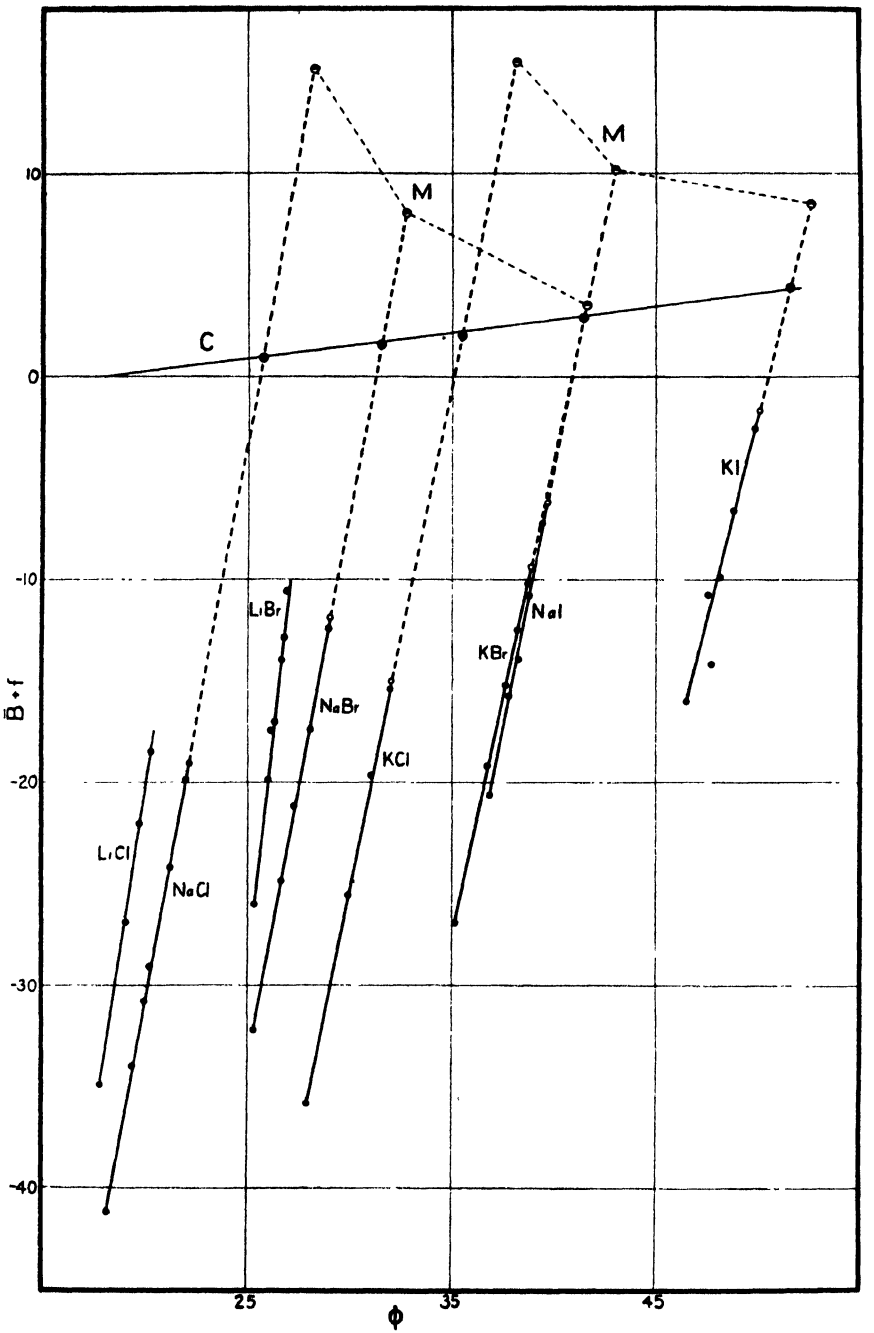

FIG. 3. PLOT SHOWING THE LINEAR RELATIONSHIP BETWEEN THE APPARENT COMPRESSIBILITY FACTOR ($\bar{B} + f$) AND THE APPARENT VOLUME OF THE SOLUTE AS THE SOLUTION CONCENTRATION CHANGES

concentration. Values of the coefficient $\frac{\partial \ln k}{\partial P}$ have already been given in table 3. The "constant" is equal to $(\bar{B}^0 - \frac{\partial \ln k}{\partial P} \phi^0)$. In figure 3 this linear relationship is depicted for the eight solutions for which we have the necessary data (table 1). In the direction of decreasing $\bar{B}$ and ϕ the lines have been extended only to the point where the values of the two variables correspond to those derived from figures 1 and 2 for infinitely dilute solution, $c = 0$. The other extreme of the actual solution state, the saturated solution, is indicated on each line by an open circle.

In taking up the examination of this graph we shall consider first an interpretation of the plotted terms. The apparent volume is usually regarded as equal to the volume of the solute (ϕ^*) minus the contraction (κ) undergone by the solvent:

$$\phi = \phi^* - \kappa \tag{7}$$

The mechanism of the contraction is not clearly established. By some investigators it is represented as a compression of the solvent (electrostriction theory), and by others as a change in the grouping of the water molecules (polymerization theory and structural theory). Since the volume of the solute is supposed to be practically constant, the change in ϕ with concentration would have to be attributed to a change in κ. From the viewpoint of even this simplified picture of ϕ, the $\bar{B}$ concept is relatively complex. The magnitude of the calculated quantity $\bar{B}\left[= -\frac{\partial \phi}{\partial P}\right]$ may be looked upon as the net result of three different effects produced by pressure: (1) a decrease in the contraction $\left(-\frac{\partial \kappa}{\partial P}\right)$ which would act to increase ϕ and which probably overshadows the other effects; (2) a decrease in the domain of the solute $\left(-\frac{\partial \phi^*}{\partial P}\right)$ which would tend to decrease ϕ; and (3) an increase in the concentration which normally produces an increase in ϕ. The increase in ϕ which results from this increase in concentration is, as has already been pointed out, equal to the factor f. Hence the plotted term $(\bar{B} + f)$ represents only the resultant of the two effects described above under (1) and (2).

With regard to these two opposing effects some further qualitative comments may be made. The magnitude of the contraction κ is conceivably determined by the properties of the individual ions, by the amount of the solvent affected, and by the state of the solvent. If pressure altered only the last factor (e.g., decrease in polymerization), it is conceivable that the resulting change $\left(-\frac{\partial \kappa}{\partial P}\right)$ would be proportional to the initial value of the

contraction. The magnitude of the variation in the domain of the solute $\left(-\frac{\partial\phi^*}{\partial P}\right)$ would depend primarily on the nature of the environment (oppositely charged ions or solvent molecules) and would therefore vary with concentration. It may be remarked here also that positively and negatively charged ions might differ considerably in their action on the water. Such a difference would be reflected in the magnitude of the quantities κ, $\frac{\partial\kappa}{\partial P}$, and $\frac{\partial\phi^*}{\partial P}$.

On the basis of the foregoing interpretation of the plotted terms it will be of interest to consider certain features of the graph. We may look upon the infinitely dilute solution as the simplest state because of the absence of the complicating interionic effects, but even here a definite analysis of the "apparent" concepts faces obvious difficulties. Thus, although the contraction presumably has a maximum value, its magnitude is unknown. Similarly, the significance of the various $\bar{B}^0$ values is obscure because the value of neither component factor is known. Attention should perhaps be called to the fact that both the ϕ^0 and $\bar{B}^0$ values of the solutions of the two lithium salts are abnormally high, if the solutions of the sodium and potassium salts can be regarded as normal. This irregularity is undoubtedly associated with the assumed existence of chemically hydrated lithium ions. In this case if the limited amount of water of hydration has undergone a large contraction, it must be supposed that the hydrated ion has less effect on the solvent than the simple unhydrated ion would have.

The existence of a linear relation between $\bar{B} + f$ and ϕ is somewhat puzzling because it means that the changes in κ and the net change in $\left(-\frac{\partial\kappa}{\partial P} + \left(-\frac{\partial\phi^*}{\partial P}\right)\right)$ resulting from a change in concentration are proportional over the entire concentration range of solution. This statement of the relationship would be quite understandable if the $\frac{\partial\phi^*}{\partial P}$ term were independent of concentration because of the possible direct dependence of $\frac{\partial\kappa}{\partial P}$ on the magnitude of κ. To take account of the presence of the $\frac{\partial\phi^*}{\partial P}$ term it would be necessary to assume that the variation in this term also is directly proportional to κ. A possible mechanism can be pictured as follows. It may be supposed that only the solvent molecules in direct contact with an ion are involved in the contraction of the solvent. It may be imagined further that with increasing concentration of the solution, these molecules are partially replaced by oppositely charged ions, resulting in a decrease in κ and a variation in the magnitude of $\frac{\partial\phi^*}{\partial P}$. If these two effects were pro-

portional to the number of solvent molecules displaced, then the $\frac{\partial \phi^*}{\partial P}$ factor might, like $\frac{\partial \kappa}{\partial P}$, be proportional to κ. In short, this argument would lead to the conclusion that the slopes $\frac{\partial \ln k}{\partial P}$ of the lines drawn in figure 3 are the sum of two proportionality factors, one representing the relationship between κ and $\frac{\partial \kappa}{\partial P}$, which would be the same for all solutions, and the other, the relationship between κ and $\frac{\partial \phi^*}{\partial P}$, which would depend on the difference between the ion–ion and the ion–solvent forces. The fact that the slopes of the lines are very nearly the same would seem to be in accord with this simplified argument. An attempt to find a quantitative expression for

TABLE 5

Data bearing on the C-state

SALT	$\beta_{salt} \times 10^6$	ϕ_c^*	V_c
NaCl	4.26	25 7	50.4
NaBr	5 07	31 5	46 6
NaI	7.08	41.5	44 2
KCl	5.63	35.5	70.1
KBr	6.70	41 5	68.2
KI	8 54	51 6	76.7

$\frac{\partial \ln k}{\partial P}$ in accord with the foregoing interpretation, resulted in the following:

$$-\frac{\partial \ln k}{\partial P} = 7.48 \times 10^{-4} - (\beta_{salt} \cdot \beta_l)10^6 \tag{8}$$

Values of the slopes calculated by means of this equation, using the β_{salt} data given in table 5, are given in the last column of table 3. They are in good agreement with the values derived from the experimental data. Although the expression is of the type expected, it is nevertheless only empirical. It is a curious fact that the figure 7.48×10^{-4} is exactly the molal compressibility of pure water.

Up to this point in our discussion we have attempted to sketch an interpretation of the apparent molal compressibility concept along rather conventional lines. In this case, as with other relationships involving the "apparent" properties of solutes, a more definite treatment is out of the question until at least one of the unknown component factors can be es-

tablished with some degree of certainty. It may be of interest therefore to describe briefly a possible procedure for estimating the volume of the solute ϕ^* on the basis of the relationships we have been considering.

The problem resolves itself into an estimation of $\phi = \phi^*$ in the hypothetical limiting solution state where the number of moles of water present is zero, because in this state κ would be presumably zero. The procedure which we shall employ rests on two postulates which may be stated here: (1) the variation of ϕ and $(\bar{B} + f)$ with concentration beyond the saturated state[2] is the same as obtained in actual solution and can be represented by equations 3 and 5, respectively; and (2) the volume of the solute is independent of concentration.

Masson sought to calculate the desired limiting value ϕ^* directly. If the condition $n = 0$ is imposed (equation 1), the resulting maximum value of the apparent molal volume ϕ_m can be calculated readily with the aid of the Masson constants. The acceptance of the ϕ_m state as the desired hypothetical limiting state has been questioned (17) on the ground that the condition employed ($n = 0$) does not take into account the forces (interionic and ionic-solvent) which are effective in the solution state.

The condition which we propose to use for the estimation of the hypothetical critical state is the compressibility of the crystalline solute. The basis for this condition is to be found in the fact that a part of the ions in concentrated solutions must be in contact. It is reasonable to suppose, therefore, that these ions in contact are subject to the same mutual forces as in the crystalline state and that they tend to form aggregates of a crystalline character. Since the fraction of ions in contact increases with concentration, it may be imagined that the desired limiting state corresponds to the concentration where all the ions form part of lattice fragments. Such a supposition is not in conflict with the present theories of concentrated solutions. Its plausibility is also suggested by some of the properties of the Masson relationship. Thus, the constant k appears (16) to be a function of the crystal ionic radii. Further, it has been shown (17) that the ϕ_m values of the alkali halides are linearly related to the corresponding volumes of the crystalline salts. In this connection, too, it is perhaps significant that the compressibility of the crystalline salt can be used in equation 8.

The concentration at which the solute has the same compressibility as in the crystalline form is readily calculated. Since $(\bar{B} + f)$ is the molal compressibility of the solute and ϕ_c^* in the limiting state would be the molal

[2] Longworth (J. Am. Chem. Soc. **54**, 2748 (1932)) gives another empirical relationship between ϕ and the number of moles of water in sodium chloride solutions, which, he points out, gives directly a value of $\phi^* =$ (=22.85).

volume of the solute, it is only necessary to solve equations 3 and 5 for the concentration which satisfies the condition:

$$\frac{\overline{B} + f}{\phi_c^*} = \beta_{\text{salt}}$$

These critical concentrations of the solutions of the sodium and potassium salts have been determined in this way, using the data already given in this paper. The β_{salt} values used were from the measurements of Bridgman (3) and were recalculated to express the volume change per metric atmosphere instead of kilogram per square centimeter. The volume of the solute ϕ_c^* and the volume of the solution V_c corresponding to this concentration have also been calculated and are presented in the following table. To avoid confusion we shall designate these properties with the subscript c and shall refer to the solution at this particular concentration as the C-state. It may be remarked here that from the nature of the calculations the ϕ_c^* values have only a slight uncertainty, whereas the V_c values are in error possibly by several per cent.

Points representing these values of $(\overline{B} + f)_c$ and ϕ_c^* are plotted in figure 3. The relation between these two quantities appears to be represented quite satisfactorily by the straight line C. It is a rather curious fact that this line shows $(\overline{B} + f)_c$ to become zero when ϕ_c^* equals 18 cc., the volume of 1 mole of water. The importance of the C-state to our problem is that it furnishes us with an estimate of the minimum value of the solute volume ϕ^*. Regardless of the actual volume of the solute, its compressibility could hardly be less than that of the crystalline solid, in which state the ions are packed most closely and the repulsive forces between them are greatest. The maximum value of the solute volume would, as we have already indicated, be ϕ_m and, for the sake of comparison, these values are also plotted in figure 3. Two lines, M, are drawn through points representing salts with a common cation.

In the case of the iodides there is very little difference between the C- and M-states, a fact which enables the solute volume to be established within narrow limits. With regard to the chlorides and bromides the situation is not so simple. In the case of the bromides, however, there is one cogent argument against the acceptance of the M-state as the limiting solution state. The ϕ_m values of these salts are slightly less than the volumes of the crystalline salts, and yet the compressibility of the former is four or five times greater than the latter. Another fact in favor of the acceptance of the ϕ_c^* values as close approximations of the volume of the solute in solution is the close agreement with values found in an entirely different way. It has been shown (19) that the apparent molal volume of a salt in saturated solutions at different temperatures varies linearly with the square of the number of moles of water present in the solution. This

relationship yields a value of the solute volume ϕ_s^* for the solution state where the number of moles of water present is explicitly zero. The ratios between ϕ_s^* and ϕ_c^* are as follows:

Salt	NaCl	NaBr	NaI	KCl	KBr	KI
ϕ_s^*/ϕ_c^*	—	1 00	1 03	0.97	1.00	1.06

Some difference between the two sets of volumes would be expected because the ϕ_s^* values correspond to solutions at different and unknown high temperatures. The effect of temperature would not be expected to be very great, and therefore the fact that the ratios given above are not far from unity is further evidence in support of our interpretation of the ϕ_c^* values.

An objection to our determination of the C-state might be found in the manner in which the compressibility coefficient of the solution varies with concentration in this hypothetical region of the solution state. According

TABLE 6

Data for the comparison of the C-state and β_{min}

SALT	CONCENTRATION OF C-STATE	CONCENTRATION OF β_{min}	β AT C-STATE	β AT β_{min}	VALUES OF f AT C-STATE
NaCl	19.6	14.0	21.0	18.9	0 82
NaBr	21.5	18 5	15.9	15.4	0 50
NaI	22.6	25 0	11.7	11 0	0.22
KCl	14.3	13.0	22.3	22.0	0.84
KBr	14 7	16.0	19.2	19.1	0 52
KI	13.0	23 0	18 8	15.0	0.47

to equation 6 the coefficient of each solution passes through a minimum. Since this fact may be of importance to our argument, the necessary data are tabulated in table 6. A comparison of the concentrations corresponding to the C-state and the minimum in the compressibility coefficient shows that for three of the salts the C-state is in a region where β is increasing with concentration. If this condition is physically unreal, then the extrapolation of Masson's and the derived relationships to the C-state would be of questionable legitimacy. On the other hand, the choice of $\beta_{min.}$ for the limit of the solution state yields negative values of $\bar{B} + f$ which are also absurd physically. It is difficult to decide how much significance is to be assigned to a minimum in the compressibility coefficient of a binary mixture, because a change in concentration produces a change in the amounts of both solute and solvent in a unit of volume. Perhaps a less obscure factor would be the compressibility of a volume of a solution con-

taining 1 mole of solute (βV), because the variation which it undergoes with a change in concentration could be ascribed primarily to the loss of solvent. For the solutions under consideration, this property, the molecular solution compressibility, passes through a minimum at concentrations greater than those of the C-state. As a matter of fact, in the case of the sodium salts the concentrations of these minima and those of the C-state are almost the same. With regard to the factor f, which is a function of both the compressibility and the concentration, the following brief account may be given. As can be seen from the data in table 1, f with increasing concentration increases rapidly at first and then tends to approach a constant value. In the hypothetical region of the solution f begins to increase again quite sharply, the point of inflection occuring very nearly at the same concentration as the minimum in β. Values of f at the C-state are included in table 6, and, with the exception of the figures for the chlorides, they are not very much larger than the values of f in the saturated solution. For the sake of completeness this table includes values of the minimum value of β and also the β value at the C-state, as calculated by equation 6.

Because of the doubt which the compressibility minima cast on the significance of the ϕ_c^* values, especially in the case of the chlorides, additional evidence in support of the calculated solute volume of sodium chloride is quite welcome. From the standpoint of our interpretation of the apparent volume as expressed by equation 7, the solute volume becomes equal to the apparent volume when the contraction κ becomes zero. Our procedure for the calculation of ϕ_c^* was based on the assumption that when no solvent is present in the solution, κ must equal zero. There is another way in which κ can be made negligibly small or zero. In accordance with the polymerization or structural theories of water we may postulate that the contraction results only from a change of the complex molecular state to a simple molecular state. Increase in pressure is supposed to reduce the number of complex molecules and thereby to act to diminish the magnitude of the possible contraction. It is this process which we have supposed to be the cause of the increase in the apparent volume with pressure. By increasing the pressure on a solution system sufficiently, the fraction of the complex molecules present should approach zero, and the apparent volume should accordingly approach a constant limiting value which we would identify as the solute volume. Data with which to test this argument are to be found in the extensive series of measurements made by Adams with sodium chloride solutions at 25°C. The apparent molal volume at infinite dilution varies with pressure as follows:

Pressure in atmospheres	1	2000	5000	7000	8000	9000	10,000
ϕ^0 in cc	17.0	21.9	24.4	25.2	25.3	25.4	25.5

These volumes show the expected variation with pressure. From the graph (figure 8) given by Adams (1) the limiting value would appear to be slightly less than 25.7 cc., which is the value of ϕ_c^* calculated for sodium chloride. The agreement between the two entirely different estimations of the solute volume can be looked upon as support of our interpretation of the ϕ_c^* values. In this connection it is noteworthy that the volume of the crystalline salt at high pressures is not very different from the solute volume. According to Adams' graph the volume of the salt becomes 25.8 cc. under a pressure of 1.2×10^3 atmospheres instead of 27.0 cc. at atmospheric pressure. At this high pressure there remains practically no free space in the crystal lattice, and the volume of the salt must be very nearly that of the domains of the constituent ions.

In view of the possibility that the calculated ϕ_c^* values might represent the volume of the solute in solution, it will be of interest to consider briefly some of the conclusions to which they lead. In the first place it should be noted that the ϕ_c^* values are additive; thus, the differences between the three anions are:

M	MBr − MCl	MI − MBr
	cc	*cc*
Na	5.8	10 0
K	6 0	10 1
Calculated	5 6	9 9

This particular set of differences is given because it affords a clue to the meaning of the term "volume of solute." If we assume that the anions have the same radii as in the crystal lattice, then the differences found are practically the differences in volumes of cubo-octahedra circumscribed about the ionic spheres. These calculated differences are given in the last row of the above tabulation. This outcome is in accord with the supposition (17) that the volume of the solute in solution is the domain of exclusion, the space within which adjacent ions or water molecules do not penetrate. If for the purpose of calculation we assume that the anion volumes are the volumes of these cubo-octahedra, then the volumes of the cations in the different salts are as follows:

	Chloride	*Bromide*	*Iodide*	*Cube*	*Cubo-octahedron*
Na	3.6	3.8	3 9	4.2	3 2
K	13 4	13 8	14 0	11 4	8 8

Two different calculated volumes of the crystal ions are also given to show that the order of magnitude of the cation volumes in solution is what might be expected if they are the domains of exclusion of the crystal ions.

The domain of exclusion of an ion probably depends somewhat on whether the ion is surrounded by oppositely charged ions (C-state) or water molecules (infinite dilution). If we assume, however, that the change is negligibly small, then according to equation 7, the difference $\phi_c^* - \phi^0$ is equal to the maximum contraction which the water undergoes as a result of the ionic forces. Values of this contraction are given below:

Salt. . . .	NaCl	NaBr	NaI	KCl	KBr	KI
$(\phi_c^* - \phi^0)$ in cc	7 5	6.2	4.6	7.6	6.3	5.1

A scrutiny of these figures reveals at once that κ depends only on the anion involved. This could mean that sodium and potassium ions produce no contraction or that they produce the same contraction. No decision between these alternatives can be made at this time. That there is a decided difference between the influence of the cation and anion and that the influence of the latter is predominant has been conjectured by several investigators on other grounds.

Using these figures for the contraction of the solvent, it is possible to carry out a number of interesting calculations. For instance, fairly good estimates can be made of the number of water molecules affected and also of the compressibility of the solute domain in infinite dilution. These suggested calculations have been made and yield quite plausible results. There is no point in considering them, however, until the interpretation of the basic ϕ_c^* values is better established.

In concluding this study a brief reference will be made to earlier work dealing with the compressibility of solutions. Röntgen and Schneider (14) proposed a simple formula for the variation of β with percentage concentration of salt in solution. For a time they believed that at the upper limit of the solution state (per cent salt = 100), β became equal to β_{salt}. This view is of interest because our calculation of the C-state makes use of the same assumption in a somewhat different form.

In 1897 Gilbault (8) published the results of an extensive series of compressibility measurements of salt solutions at 20°C. over the pressure range 0 to 300 atmospheres. He concluded that the variation of the compressibility could be represented by an expression which may be written as follows:

$$\frac{(\ln \mu_0 - \ln \mu)d}{a \cdot d_1} = k$$

where μ_0 = the compression of 1 mole of water $\frac{18}{d_1}\beta_1$

μ = the "molecular compressibility" of the solution. If we let ν = number of ions per molecule of salt, N = moles of

water per mole of salt, and c = concentration in moles per liter, then

$$\mu = \frac{1000}{c(N + \nu)} \cdot \beta$$

$$a = \frac{\nu}{N + \nu}$$

d, d_1 = densities of solution and pure water, respectively.

k = a constant characteristic of each salt.

The significance of this equation lies in the utilization of μ, which gives the volume change of an amount of solution that contains always the same total number of water molecules and ions.

Gilbault calculated the values of k for eighteen salt solutions and found them to be constant within 0.3 per cent over a wide concentration range. Permann and Urry (12) recently tested the equation with their compressi-

TABLE 7

Variation of calculated values of k with concentration

SALT	CONCENTRATION	k (CALCULATED)	SALT	CONCENTRATION	k (CALCULATED)
NaCl	5 008	1 518	NaBr	7 396	1.667
	3 246	1 492		4 099	1 461
	1 657	1 446		2.307	1 268
	1 087	1 401		1 206	1 237
	0 497	1 329			

bility data for solutions of sucrose, urea, potassium chloride, and calcium chloride over the temperature range 30–80°C. and found that the agreement between the calculated and observed values of β "is surprisingly good considering the range of concentration covered. It suggests that dissociation is complete in electrolytic solution, thus confirming the theory of Debye and Hückel." On the other hand, a test of Gilbault's equation with our data reveals the equation to be quite unsatisfactory. For example, as can be seen in table 7, the calculated values of the characteristic constant vary markedly with concentration. Curiously enough, practically constant values of $k = 1.562$ are obtained for the chloride solutions if the compressibility of water is taken equal to 42.4×10^{-6} instead of 41.8×10^{-6}. But in order to get fairly constant k values for the bromide solutions a still higher value for β_1 (43.6×10^{-6}) must be assumed. This result would indicate that the original equation is insufficient to represent the variation of β with composition and density of the solution and that the equation requires another factor, constant for each solute, added to the

term. The only other criticism to which Gilbault's equation has been subjected was made by Tamman (21), who pointed out that the experimental precision claimed by Gilbault would mean that the temperature of his thermostat bath was held constant to within 0.0001°C. Tamman estimates that the actual uncertainty in Gilbault's data amounts to 1 to 3 per cent and in some cases may be even greater.

The reason for considering Gilbault's equation in such detail is the relationship between the "constant" k and our factor $\bar{B}^0$. Taking μ_0 equal to $V_1\beta_1$ and μ equal to $(1 - a)\, V_1\beta_1 - \frac{a\bar{B}^0}{\nu}$, we can write Gilbault's expression as

$$\bar{B} = V_1\beta_1\nu\left(\frac{1 - e^{-ka\frac{d_1}{d}}}{a} - 1\right)$$

Since at infinite dilution a approaches 0, we have

$$\bar{B}^0 = V_1\beta_1\nu\,(k - 1)$$

In other words, for a series of salts of the same valence type $\bar{B}^0$ should be linearly related to the Gilbault constant k. The values of $\bar{B}^0$ calculated from the k values given by Gilbault cannot be compared with our $\bar{B}^0$ values because of the difference in temperature involved. However, the difference between the two sets of $\bar{B}^0$ values is not only too large to be attributed solely to the effect of temperature but depends in magnitude on the cation of the salt. If we use the information obtained from our data for sodium chloride solutions ($k = 1.562$ when $\beta_1 = 42.4 \times 10^{-6}$), $\bar{B}^0$, calculated by the above equation, is 39.8×10^{-4}. This figure is not exactly the same as that (41.2×10^{-4}) given in table 1 but the difference may arise from the fact that the last figure applies to systems under 200 atmospheres, whereas the other has not been calculated so rigorously. In any case it may be concluded that Gilbault's equation in the original form is too simple and that the introduction of another factor as was suggested above may perhaps remedy the difficulty.

SUMMARY

Evidence is presented to show that Masson's equation $\phi = kc^{\frac{1}{2}} + \phi^0$ is applicable to solution systems under pressures of 200 metric atmospheres.

The relationship between the apparent molal compressibility and the concentration is derived from Masson's equation. This relationship is used to determine the apparent molal compressibilities of solute at infinite dilution $\frac{\partial\phi^0}{\partial P}$, which are shown to be additive, and also the values of $\frac{\partial k}{\partial P}$ for different solutions.

By combining the apparent compressibility relationship with Masson's equation an expression is obtained which gives the compressibility coefficient of the solution (β) as a function of concentration.

The significance of the variation of the apparent compressibility with the apparent volume is considered from the standpoint of the contraction of the solvent resulting from the effect of the solute. . On the basis of these considerations the volume of the solute in solution is calculated on the assumption that the limit of the solution state is reached when the compressibility coefficient of the solute in solution equals that of the crystalline salt. Although these hypothetical calculated volumes are subject to some qualification, they are shown to be of the expected order of magnitude and to be additive. The use of these solute volumes leads to the conclusion that the cations (Na^+, K^+) produce the same or no contraction of solvent, and the anions cause a contraction which decreases in the sequence Cl^-, Br^-, I^-.

The single constant of Gilbault's equation, which relates the compressibility coefficient of a solution to the density and percentage composition, is shown to be a simple function of $\frac{\partial \phi^0}{\partial P}$ and the valence type of the electrolyte. However, a test of Gilbault's equation indicates that it is not valid in the original form and that the introduction of a second constant is perhaps necessary.

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THE VISCOSITY AND FLUIDITY OF LITHIUM CHLORIDE IN ACETONE SOLUTION

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The viscosity of aqueous electrolyte solutions is occupying considerable attention at the present time. The empirical equation put forward by Jones and Dole (9) relating the relative fluidity, $\varphi_r = \varphi_c/\varphi_0$, to the square root of the concentration, c (in moles per liter),

$$\varphi_r = 1 - A\sqrt{c} + B \cdot c + \ldots$$

has been theoretically derived from considerations of the Debye-Hückel theory (3, 4, 5, 14), and the Falkenhagen constant "A" for a dozen electrolytes has been evaluated experimentally through numerous recent measurements (7, 8, 10, 11, 15) and the interpretation of some earlier viscosity data (1, 6, 13).

In the course of some investigations in progress in this laboratory, we found occasion to measure the viscosities of solutions of lithium chloride in acetone with sufficient accuracy to warrant interpretation of our results in the light of the interionic attraction theory as a test of the Falkenhagen equation when applied to non-aqueous solution.

EXPERIMENTAL

Apparatus

The viscometer has been previously described (7). The probable error of a determination of relative viscosity as the average of a pair of observations (from four determinations of the viscosity of acetone involving twelve observations) is, by the method of least squares, 0.02 per cent.

Materials

The lithium chloride used was "Baker's Analyzed;" it was recrystallized from conductivity water, dried, crystallized from purified acetone, and dried. The acetone used was "Coleman and Bell's C.P.;" it was distilled from alkaline permanganate, dried over anhydrous calcium chloride, and slowly redistilled. Its boiling point was 55.05°C. at 735.4 mm. (uncorrected).

Solutions

Solutions were made up by weight, the dilute solutions being made by weighing in additional acetone to a weighed portion of a more concentrated solution. The solutions were kept in closely stoppered Pyrex flasks in a dark closet; the viscosity of the most concentrated solution measured at the end of the experiments agreed with the viscosity measured at the beginning within the limit of experimental error. Concentrations were calculated to moles per kilogram of solvent, m.

Densities

The densities of acetone at 18 and 25°C. were determined as 0.7923 and 0.7844. The densities of three solutions were determined at 25°C. as follows:

m	ρ
0.1726	0.7905
0.2591	0.7932
0.3454	0 7967

These values established the relation:

$$\rho_{25} = 0.7844 + 0.036m$$

In view of the relatively small temperature interval of 7°C., constancy of the partial molal volume of lithium chloride was assumed, whence:

$$\rho_{18} = 0.7923 + 0.036m$$

From these densities, the concentrations were calculated to moles per liter of solution, c.

Data

The experimental results are summarized in table 1.

INTERPRETATION OF RESULTS

When the values of $(\eta - 1)/c$ were plotted as ordinates against the corresponding values of c as abscissas, a pair of concave sagged curves were obtained which exhibited minima at about 0.16 mole per liter. While $(\eta - 1)/c$ is strictly the slope of the chord connecting a point on the viscosity–concentration curve with the origin, it approximates the slope of the curve at the point; thus the initial downward slope of these curves corresponds to negative curvature in the η–c curves, and the minimum to a point of inflection in the latter. These plots of the "Grüneisen function" emphasize that the negative curvature of the η–c curve is more pronounced at the higher temperature, in contrast with the behavior of electrolytes in aqueous solution (1).

When the values of $(\varphi_r - 1)/\sqrt{c}$ were plotted as ordinates against the corresponding values of $\sqrt{c}$ as abscissas, the points located a pair of *approximately* straight lines which intersected the axis of $(\varphi_r - 1)/\sqrt{c}$ between -0.02 and -0.03. The "best" straight lines through the points were established by the method of least squares as:

$$(\varphi_r - 1)/\sqrt{c} = -0.0213 - 0.423\sqrt{c} \text{ at } 18°\text{C.}$$
$$(\varphi_r - 1)/\sqrt{c} = -0\ 0349 - 0.382\sqrt{c} \text{ at } 25°\text{C.}$$

The deviations of the fluidities calculated by these equations from the observed fluidities were considerably greater than the probable error of

TABLE 1

Viscosity and fluidity of lithium chloride in acetone

NO OF RUNS	c	ρ	$\eta_c/\eta_0 = \eta$	$(\eta - 1)/C$	$\varphi_c/\varphi_0 = \varphi_r$	$\sqrt{c}$	$(\varphi_r - 1)/\sqrt{c}$	φ_c rhes
				At 18°C.				
3	0 2739	0 8046	1 14535	0 531	0 87309	0 5234	−0.2425	268.3
3	0 1368	0 7984	1.0711	0.520	0.93362	0.3699	−0 1795	286.9
4	0 07771	0.7958	1.0435	0.560	0.95830	0.2788	−0.1496	294.5
3	0 03429	0.7939	1.0211	0.615	0.97934	0.1852	−0.1116	301.0
3	0 00863	0.7927	1.0055	0.637	0.99453	0.0929	−0.0589	305.6
4	0.00431	0 7925	1.0027	0.626	0.99731	0 0657	−0.0410	306.5
10	0	0 7923	1.0000		1.00000			307.31
				At 25°C.				
5	0 2712	0 7967	1.1402	0 517	0.87704	0 5208	−0.2361	288.15
3	0 13545	0.7905	1.0685	0.506	0.93589	0.3682	−0 1742	307.5
4	0 07694	0.7879	1.0421	0 547	0.95959	0.2774	−0 1457	315.3
3	0.03395	0.7860	1.0193	0 596	0.98106	0.18425	−0.1028	322.3
4	0 00854	0.7848	1.0052	0.609	0.99483	0.0924	−0.0559	326.85
12	0	0 7844	1.0000		1.00000			328 55

the measurements—about 0.15 per cent on the average—and showed a definite trend indicative of curvature. Assuming the validity of the equation of Jones and Dole,

$$\varphi_r = 1 - A\sqrt{c} - B \cdot c$$

the value of the Falkenhagen constant is 0.028, on the average.

Plotting $(\varphi_r - 1)/\sqrt{c}$ against $\sqrt{c}$, and $(\eta - 1)/\sqrt{c}$ against $\sqrt{c}$ on large sheets of coördinate paper, and fitting spline curves through the points, we obtained 0.024 as the graphical value of the constant at both temperatures. E. L. Vernon has privately communicated a calculated value, 0.0237 at 25°C. (cf. reference 5).

In order to bring out the inflection of the η–c curves, a function was sought which would emphasize the curvature without introducing the objectionable feature of the Grüneisen function, i.e., that the points located by small values of c become exceedingly sensitive to experimental error and tend to scatter. Such a function was found when the divergences of the observed fluidities (in rhes) from ideality were tabulated against the corresponding concentrations (table 2). The fluidity which the solution would have if it were ideal was calculated by Bingham's equation (2):

$$\Phi = \alpha\varphi_1 + \beta\varphi_2$$

where φ_1 is the fluidity of acetone and α its volume fraction in the solution;

TABLE 2

The values for the differential function, $\Delta\Phi$

c	Φ (IDEAL)	φ_c (OBSERVED)	DIFFERENCE	DIFFERENCE — 100c
		At 18°C.		
0.2739	305 6	268 3	37.3	9.91
0.1368	306 45	286 9	19.55	5.87
0.07771	306 8	294.5	12.3	4.53
0.03429	307.1	301 0	6.1	2 67
0 00863	307.25	305 6	1 65	0 79
0 00431	307 3	306 5	0.8	0 37
0	307 3	307 3	0 0	0 00
		At 25°C.		
0.2712	326 5	288.15	38.35	11.23
0 13545	327.5	207.5	20.0	6.455
0.07694	328.0	315 3	12.7	5.01
0.03395	328.3	322.3	6.0	2.60
0 00854	328 5	326.85	1.65	0.80
0	328 55	328 55	0 0	0.00

the fluidity of lithium chloride (solid), φ_2, is zero. Fluidities are plotted as a function of concentration in figure 1; the straight lines show the theoretical additive fluidity relationship. The slopes of the theoretical fluidity curves are computed from the solution containing 0.3454 mole of lithium chloride per kilogram of acetone: 0.2739 and 0.2712 mole per liter of solution at 18 and 25°C., respectively. The salt has a (dry) volume of 7.09 cc., the acetone a volume of 1262.15 cc. at 18°C. and 1274.86 cc. at 25°C. The volume fractions of acetone are therefore 0.9944 and 0.9937, and the fluidities (0.9944 × 307.3 =) 305.6 and (0.9937 × 328.55 =) 326.5 rhes at the two temperatures, respectively.

When values of $\Delta\Phi = \Phi - \varphi_c - 100c$ were plotted as ordinates against corresponding values of c as abscissas, an exaggeration of the curvature of fluidity–concentration curves was effected, which clearly marked the point of inflection at 0.16 mole per liter (see figure 2).

The marked positive curvature of the φ–c curves may be interpreted as evidencing some sort of combination between solvent and solute, which

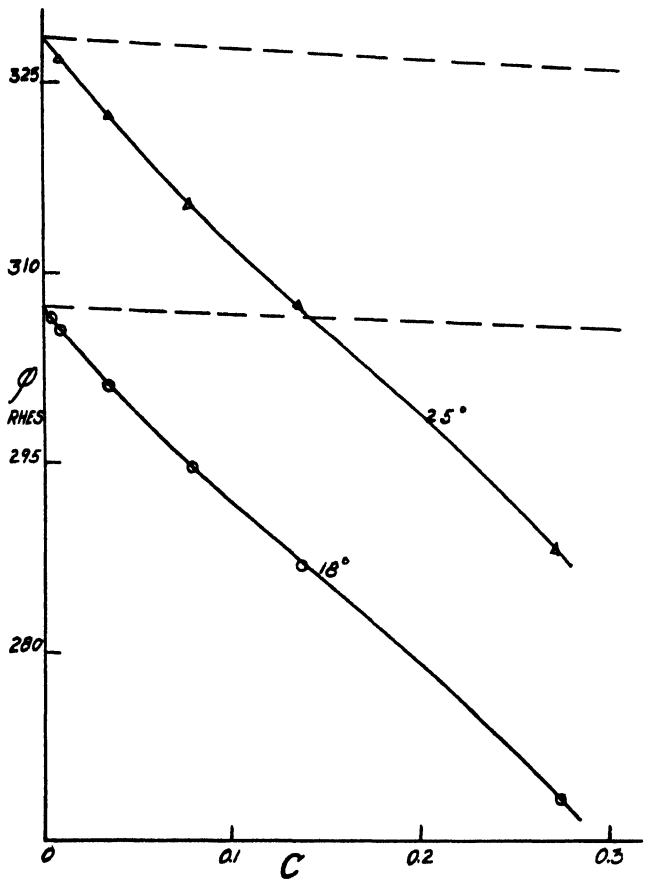

FIG. 1

we may call solvation. Another evidence for solvation was adduced by a consideration of the partial molal volume. Using the densities measured at 25°C. and the equations of density derived therefrom, the apparent molal volume was computed for lithium chloride in solutions containing 1000 g. of acetone and n_2 moles of salt, over the range of concentration $n_2 = 0$ to $n_2 = 0.5$ by means of the defining relation (12):

$$\xi = \frac{(V - n_1 v_1)}{\ldots}$$

Plots of ξ against n_2 and plots of ξ against log n_2 gave values of $\bar{v}_2$, the partial molal volume of lithium chloride, ranging from -5.0 cc. at infinite dilution to practically constant values of -4.0 cc. at 18°C. and -4.3 cc. at 25°C., over the range of concentration covered by viscosity measurements.

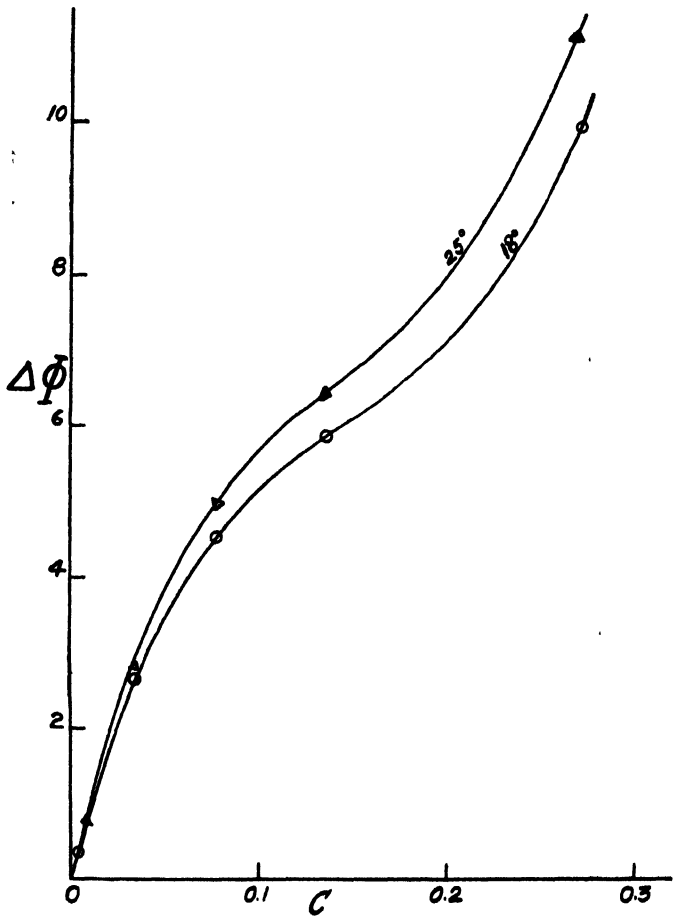

FIG. 2

The departure of the fluidity curves from ideality (figure 1), apparently measures the resultant of three factors: (1) the stiffening effect due to interionic attraction, (2) the increase in fluidity due to dissociation (1) of molecular complexes which may be supposed to exist in acetone as a pure phase, and (3) the decrease in fluidity due to solvation. By making certain assumptions, however, "apparent solvation numbers" may be calculated; consideration of these numbers appears worthy of notice.

The stiffening effect may be calculated from the Falkenhagen relation,

$$\eta = \frac{\eta_c}{\eta_0} = 1 + A\sqrt{c} + \cdots$$

which transforms into

$$\varphi_c = \varphi_0 - A\sqrt{c}\,\varphi_c - \ldots$$

where φ_0 and φ_c are the fluidities of solvent and solution (in rhes), respectively. The value of φ_c is assumed to be the fluidity of the ideal solution at the concentration c, since the Falkenhagen relation has been shown to hold in very dilute solution, and effects of dissociation and solvation are neglected. In the solution containing 0.3454 mole of lithium chloride per kilogram of solvent, there is 0.2712 mole per liter of solution at 25°C.; the observed fluidity is 288.15 rhes. This is a decrease of 38.35 rhes from the ideal fluidity, 326.5 rhes. Of this decrease, ($A\sqrt{c}\,\varphi_c$ =) 4.71 rhes is due to interionic attraction. To yield a fluidity of (288.15 + 4.71 =) 292.86 rhes in ideal solution, since

$$\Phi = \alpha\varphi_1$$

it follows that the apparent volume fraction, α, is (292.86/328.55 =) 0.8914, while the ideal volume fraction is 0.9937—a decrease of 0.1023 or 10.3 per cent. The decrease in α is assumed to mean that 10.3 per cent of the acetone combines with lithium chloride to form a solvate. Since in 1000 g. of acetone there are 17.23 moles, 1.775 moles of acetone unite with 0.3454 mole of lithium chloride, an apparent solvation number of 5.14. Solvation numbers calculated similarly for the four most concentrated solutions gave as the average value 5.57 ± 0.17 at 18° C. and 5.21 ± 0.12 at 25°C., without trend. The approximate constancy of the degree of solvation is in accord with the approximate constancy of the partial molal volume.

While these numbers represent the resultant of two opposed effects, solvation tending to decrease the fluidity and dissociation of $(CH_3COCH_3)_x$ complexes tending to increase the fluidity, they approximately measure the solvation effect; for the degree of association, σ, for acetone is small in comparison with water, and the temperature coefficient of viscosity for acetone being small, it may be assumed with a high degree of probability that the increments of fluidity at 18 and 25°C. due to change in the value of σ effected by the solute are nearly equal,—for nearly equal numbers of $(CH_3COCH_3)_x$ complexes come within the sphere of influence of the solute particles at both temperatures. Thus the apparent solvation numbers are nearly proportional to the true degree of solvation.

SUMMARY AND CONCLUSION

Measurements have been made on the viscosity of acetone solutions of lithium chloride at 18°C. over the range 0.004 to 0.274 mole per liter, and at 25°C. over the range 0.008 to 0.271 mole per liter.

The stiffening effect on the solution due to the electric forces of the ions in tending to maintain a space lattice structure has been observed. The value of the constant A obtained compares favorably with the theoretical value as calculated by Falkenhagen and Vernon.

Fluidity–concentration curves are shown to be highly inflected. It is suggested that the complexity of the fluidity–concentration relationship expresses the resultant of three factors: interionic attraction—most effective at extreme dilution—and a solvation effect superimposed upon the effect which a solute itself exerts in decreasing the fluidity of the pure solvent.

Evidence for solvation is adduced, and measures of the degree of solvation are obtained.

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NEW BOOKS

Conduction of Electricity Through Gases. By SIR J. J. THOMSON AND G. P. THOMSON. Third edition, Volume II. 608 pp. Cambridge: Cambridge University Press, 1933. New York: The MacMillan Company, 1933. Price: $6.50.

The volume treating ionization by collision and gaseous discharge completes the third edition of this well-known work originated by Sir J. J. Thomson.

In spite of, or rather because of, the vast amount of material dealt with, the reviewer gets the impression that this, the third edition, cannot occupy the commanding position which the first edition did thirty years ago in the then much newer and narrower field of electrical discharge in gases. This is not meant as a criticism of the admirable compilation. The field presents so many possibilities and complexities that it has expanded enormously in various directions, experimental and theoretical. It is no longer possible to give equally adequate treatment to all the phases of the subject in the compass of two volumes. The task is not rendered easier by the fact that physics has been making major advances along a broad front with such rapidity that the conquered terrain has not yet been properly cleared up and unified in a way that makes a complete survey possible.

The volume is written in a clear readable style. The figures and tables are well presented. The first two chapters are devoted to cathode rays, the second to their wave properties, the third to electron collisions, the fourth and sixth respectively to ionization by positive ions and by x-rays, the fifth to reflected and secondary electrons from solids, the seventh to ionization by chemical reaction, the material of which is little changed from the earlier edition. Chapter VIII, of more than one hundred and fifty pages, deals with the various phenomena of gaseous discharge at low pressure. Chapters IX and X deal with the spark and the electric arc.

S. C. LIND.

The Physico-chemical Properties of Plant Saps in Relation to Phytogeography. Data on Native Vegetation in its Natural Environment. By J. ARTHUR HARRIS, late Head of the Department of Botany, University of Minnesota. Formerly Resident Botanist, Station for Experimental Evolution, the Carnegie Institution of Washington. 13.5 × 23.5 cm.; vi + 339 pp. Minneapolis: The University of Minnesota Press, 1934. Price: $4.50.

From about 1912 until his death in 1930 one of Dr. Harris' major projects was the investigation of the relationship which existed between the physicochemical properties of the leaf tissue fluids of plants and the ecological environment characteristic of the plants. He devised methods and apparatus suitable for the carrying out of physicochemical technics in field laboratories, and established his laboratories in the field where plants could be studied in their native habitats. Extensive studies were carried out on the mesophytic plants of Long Island, N. Y., the coastal plains and sand dune areas of North and South Carolina and the Island of Jamaica, the Dismal Swamp in Virginia, the Everglades and coastal swamps of Florida and Georgia, the rain forests of Jamaica and Hawaii, and the deserts, mountain slopes, arroyos, salt flats, lava fields, dunes, etc., of Arizona, Utah, California, Colorado, Washington, and Hawaii. Altogether sixteen seasons were spent in the field studies. Fragments of the data were published by Dr. Harris from time to time but the great masses of

data were kept for later monographic treatment. Accordingly at the time of his death many thousands of original records remained unpublished.

A committee of his colleagues, consisting of Dr. C. O. Rosendahl, Dr. G. O. Burr, and the reviewer, were charged by President Coffman of the University of Minnesota with the task of examining the various papers of Dr. Harris and bringing to the point of publication such data as could be salvaged. The present volume is the first result of this undertaking.

After mature deliberation it was decided by the committee to publish only the "raw data" and not to attempt an analysis of the interrelationships of the various constants or to formulate an interpretation of the data in relation to the problems of phytogeography. This conclusion was reached partly because of the lack of close familiarity of the members of the committee with the plant associations which Dr. Harris had studied, and more especially because of the difficulty which the committee would face in attempting a discussion of such an enormous mass of varied data. It was felt that science might better be served by presenting the data in such form that they would be readily utilizable by other workers.

The volume opens with a reprint of a paper by Dr. Harris on "Physical Chemistry in the Service of Phytogeography" in which he discusses the types of problems toward the solution of which the data were collected. This is followed by a detailed "project outline" which he had prepared while soliciting funds for the intensive prosecution of the project, and which is accompanied by a bibliography of the forty-four papers which he had published in this field. This bibliography is followed by a contributed paper by Dr. H. L. Shantz on "The Importance of Phyto-chemical Studies in the Field of Plant Geography." This section of twenty-four pages introduces "The Experimental Data," which is essentially a single table occupying one hundred and seventy-six closely printed pages. The data are arranged alphabetically by states and within each state by the botanical names of the plants which were studied. Thus no botanical index to the volume is necessary. Physicochemical constants on more than 12,000 series of plant collections are tabulated in this section. The items recorded in the various columns are: (1) botanical name of the plant studied; (2) chemical number (a code number showing year of collection and other essential data); (3) the "station number" (a code number referring to a later "station description;" (4) the depression of the freezing point of the sap in degrees Centigrade; (5) the osmotic pressure of the sap in atmospheres calculated from Δ; (6) the specific electrical conductivity of the plant sap expressed in mhos; (7) the chloride content of the sap expressed as grams of chloride ion per liter; (8) the sulfate content of the sap similarly expressed; and (9) the pH of the sap.

Following this tabulation there are seventy-seven pages of "station descriptions," in which the geographical and botanical characteristics of the locality where the collections were made are noted. These descriptions are sufficiently exact so that another worker visiting the region should have no great difficulty in locating approximately the spot where collections were taken. These descriptions, many hundreds in total, are accompanied by a notation of the "chemical numbers" of samples taken for analysis.

The volume closes with a "chemical number" index through which those interested are enabled to find the various chemical data listed for all plants which may be growing together in any selected "station" or habitat.

The entire volume may be regarded as one enormous table of physicochemical data on plant saps. Unquestionably it contains more original data on this subject than may be found in all the rest of the literature. The data are presented without any discussion of their interrelationship. The volume should become a part of all

reference libraries and all physiological libraries. Most ecologists and many physiologists will find it a mine of information.

ROSS AIKEN GORTNER.

The Chemistry of Antigens and Antibodies. By J. R. MARRACK. Medical Research Council Special Report No. 194. 16 x 25 cm. London: H. M. Stationery Office, 1934. Price: 2s. 6d. net.

During the last decade there has been an ever-growing volume of literature dealing with the basic problems of immunity in terms of the fundamental sciences. Dr. J. R. Marrack has brought together in the small space of one hundred and thirty-four pages a fairly complete collection of the most important physicochemical researches which have directly contributed to modern views concerning the nature of antigens, antibodies, and the antigen–antibody reaction.

The first chapter is devoted to certain physicochemical considerations and consists of a short and well-written survey of current views on the shapes and sizes of molecules, intermolecular forces, the structure of proteins, and the stability of suspensions. The recent evidence for and against the protein nature of antibodies is carefully reviewed in chapter II, and later in the book the specificity of artificial protein antigens, which contain "determinative" chemical groupings, is lucidly discussed in terms of structural organic chemistry.

To the chemist entering the field of immunology this monograph can be heartily recommended, for it gives a clear account of the physical and chemical studies which have served to elucidate certain immunological reactions. To the more experienced immunologist who has already realized the value of chemical concepts in the study of immunity, Dr. Marrack's book will be especially acceptable since it contains, besides a thorough survey of the recent literature, many stimulating suggestions which will doubtless form the basis of future investigations.

W. T. J. MORGAN.

A Textbook of Inorganic Chemistry. By FRITZ EPHRAIM. Second English edition by P. C. L. THORNE. 24 x 16 cm.; xii + 873 pp. London: Gurney and Jackson, 1933. Price 28/-.

In the first English edition of this work, of eight hundred and five pages, the translator made some additions to take account of English and American needs. The present edition includes much more material from the new German edition and some additions by the translator. The latter do not always go far enough. The section on Werner's theory is very valuable and satisfactory, but the reference to the new theory of the coördinate link is far too brief. The discussion of the hydrogen–palladium system leaves the subject with Hoitsema, and the newer work of Gillespie and Hall, Hanawalt, and others, is not mentioned, so that the section is quite out of date. A similar criticism could be made of the section on silicic acids, where only van Bemmelen's work appears. The phase rule diagram of silica does not include two β-tridymites; only the old methods of preparing boron hydrides are given; and in many other places the text could usefully have been brought up to date. The translation is satisfactory, although the names of Neumann and Hauck, correctly given in the German, appear as Wennann and Hanck on p. 325, Mayer instead of Mayes on p. 528, etc. The section on the thionic acids is too sketchy. The "very interesting addition compounds (nitro-metals)" of Sabatier and Senderens mentioned on p. 611, like the compounds NO_2 and H_2O_7 on p. 637, have long since passed out of existence.

The book is one which advanced students will find very useful, but it is to be re-

gretted that the revision by the translator has not been more drastic and satisfactory. The result is, in consequence, that some parts do not give a really modern presentation of the subject.

J. R. PARTINGTON.

Chemische Technologie der Neuzeit. By OTTO DAMMER AND COLLABORATORS. Second enlarged edition in five volumes. Volume II. Part ii. 27 x 19 cm.; xvi + 888 pp. Stuttgart: Ferdinand Enke, 1933. Price: unbound, 93 M; bound, 98 M.

The present volume of this very comprehensive work deals entirely with metals: iron and steel, gold, platinum metals, aluminum, magnesium, calcium, alkali metals, beryllium, mischmetall, nickel and cobalt, silver, copper, tin, antimony, zinc, cadmium, thallium, arsenic, mercury, bismuth, lead, chromium, molybdenum, tungsten, vanadium, niobium, tantalum, titanium, uranium, manganese, rhenium, gallium, indium, and germanium. It will be seen that the rarer metals are included, but the treatment is sometimes rather brief; for example, only four and a half pages are devoted to vanadium, and only five, one a table of analyses of ores, to tungsten. The references to literature in these sections are sometimes rather scanty. The information on the magnesium and beryllium alloys is disappointingly brief. The commoner metals are more fully dealt with, one hundred and ninety-two pages being devoted to iron and steel, seventy-two to copper, and eighty-eight to lead. The various contributors have made an attempt to deal adequately with the material in the space available and have taken good account of modern literature, including English and American, and patents. In so far as a single volume can give a satisfactory treatment of such a wide range of subjects, the present work gives a comprehensive and able survey of the field. It will need supplementing by special monographs when full information on details is required. The book is well printed and illustrated and contains many tables of numerical information, including the properties of the metals.

J. R. PARTINGTON.

Practical Methods of Biochemistry. By FREDERICK C. KOCH. Cloth; 15 x 23 cm.; viii + 280 pp.; 17 fig. Baltimore: William Wood and Company, 1934. Price: $2.25.

This is a laboratory manual in physiological chemistry, with especial reference to medical school aspects. The author has for many years been in charge of the work in physiological chemistry at the University of Chicago, and the present volume affords ample evidence that the experiments have been tried over and over again in class laboratories.

The book is divided into three parts; I, The Chemistry of Cell Constituents, including chapters on carbohydrates, lipins, proteins, nucleoproteins and nucleic acids, and hydrogen-ion concentration; II, The Chemistry of the Digestive Tract, with chapters on salivary digestion, gastric digestion, intestinal digestion and bile; and III, The Blood and Urine, with chapters on blood and hemoglobin, the quantitative analysis of blood, the quantitative analysis of urine, and the chemical examination of urine in pathological conditions. The book contains an elaborate appendix of fifty-three pages in which explicit directions are given for the preparation of the various laboratory reagents. An adequate subject index closes the volume.

In all, directions for two hundred and twenty-eight laboratory experiments are given. Most of these are for qualitative tests for various biochemical compounds. Numerous quantitative procedures are, however, included. Since the book is designed for a first course in medical biochemistry, but little use is made of physicochemical

equipment or technics. This omission is the only thing that the reviewer feels calls for criticism. Since living processes are so intimately bound up with problems of osmotic pressure, permeability, electrical conductivity, and colloid behavior in general, it would seem only just that medical students should be introduced to a few simple experiments which would serve to quicken their understanding of such phenomena.

The reviewer knows of no better laboratory manual covering the field for which this text is intended.

ROSS AIKEN GORTNER

Many readers of This Journal will be interested in the following pamphlets published by Hermann et Cie., Paris. Each pamphlet contains a paper (including discussion) read at the 1933 Réunion internationale de chimie physique.

I. L'Effet Volta. By Emmanuel Dubois. 6 fr.
II. The Electrical Properties of Semi-conductors and Insulators. By M. A. H. Wilson. 4 fr.
III. On Phase Boundary Potentials. By Eric Keightley Rideal. 4 fr.
IV. Pile Metalliche. By O. Scarpa. 6 fr.
V. Das elektrolytische Kristallwachstum. By M. Volmer. 4 fr.
VI. Les Électrons dans les Métaux. Problèmes Statiques Magnétisme. By F Bloch. 5 fr.
VII Conductibilité Électrique des Isolants et des Semi-conducteurs. By A. F. Joffé. 10 fr.
VIII. Les Électrons dans les Métaux du Point de Vue Ondulatoire. By Léon Brillouin. 9 fr.
IX. Conductibilité Électrique et Thermique des Métaux. By Léon Brillouin. 18 fr.
X. Adsorption, Electro-reduction and Overpotential at the Dropping Mercury Cathode. By J. Heyrovsky. 12 fr.
XI Phénomènes Photoélectrochimiques. Action de la Lumière sur le Potential Métal-Solution. By René Audubert. 8 fr.
XII. Les Colloïdes et la Couche de Passage. By A. Gillet and N. Andrault de Langeron. 10 fr.
XIII. Sur le Potentiel Métal-Solution dans les Dissolvants Autres que l'Eau. By Paul Dutoit. 4 fr.
XIV. L'Effet Électro-thermique Homogène. By Carl Benedicks. 8 fr.
XV. Die Theorie der thermoelektrischen Effekte. Legierungen, Unvollstaendige Ketten, Benedickseffekt. By Lothar Nordheim. 6 fr.
XVI. La Notion de Corpuscules et d'Atomes. By Paul Langevin. 12 fr.

F. H. MACDOUGALL.

The Manufacture of Soda. By TE-PANG HOU. American Chemical Society Monograph No. 65. 365 pp. New York: The Chemical Catalog Co., Inc. Price: $8.00.

Dr. Hou has undoubtedly produced the first authoritative treatise on the manufacture of soda to appear in this country. The first three chapters, which are devoted to the historical development of the alkali industry, are of great interest especially to students of chemical engineering economics. They illustrate the peculiar interweaving of interests in the chemical field and the economic forces affecting the rise and downfall of a great industry. Since this is an A. C. S. monograph, it does seem unfortunate to the reviewer that more is not given of the history of the development

of the Solvay process in this country and the connection with it of such great chemical pioneers as Hazard, Pennock, Trump, and Handy.

Chapter IV, on the purification of brine, is concise and well written and, perhaps, more important than the author believes, especially in this country where the quality of the brines used differs so widely. Chapter V, on the burning of limestone, is especially timely, since this important phase of the plant operation is often neglected or its importance not appreciated. The next nine chapters are devoted to a careful detailed discussion of the operations of the ammonia-soda process. The physico-chemical factors controlling the operations are given full and complete discussion. Necessarily, the description of equipment is neither quite so complete nor so modern because of the traditional policy of secrecy in which this industry has grown. Undoubtedly, it represents Dr. Hou's observations of plant practice and equipment, which can hardly be expected to cover all the newest "wrinkles" in the latter field. The reviewer is not inclined to agree with the author's statements regarding draw temperatures on p. 102 so far as general plant practice in this country is concerned.

The last twelve chapters are devoted to special alkali products, power generation, control, losses, analyses and tests, and, finally, to an all too brief chapter on plant lay-out and design. The chapter on electrolytic caustic is brief but well done, while those concerning control, losses, and analytical procedure are most excellent. The book is exceedingly well-written, clear, and forceful. Not many errors, either typographical or otherwise, were apparent to the reviewer. On p. 176 "Table 74" in the text should read "Table 79." The workmanship and materials of the book are of the usual excellent quality of this series.

This book will be of interest to students of chemical economics, industrial chemistry, and particularly the application of physical chemistry to industrial processes. To the practical chemist or engineer in the alkali industry it offers the most complete and careful account of this field which has been produced in the English language, and a careful perusal is almost sure to stimulate even the "old-timers" with a few new and useful ideas.

RALPH E. MONTONNA.

Elektrolytische Leitfähigkeit unter extremen Bedingungen. XXXVIII. Hauptversammlung der deutschen Bunsen Gesellschaft. 28 x 20 cm.: iv + 183 pp. Berlin: Verlag Chemie, 1933. Price: 8 marks.

This volume consists mainly of papers delivered at a discussion held by the Bunsen Gesellschaft on "Electrolytic Conduction under Extreme Conditions." The topics include the effect of high frequency and voltage upon electrical conductivity, electrical conductivity in non-aqueous solvents, and phenomena associated with the conduction of electricity by solids. Prominent among the contributors are Debye, Ulich, v. Hevesy, Tubandt, Lange, and Falkenhagen.

It is an interesting and important consequence of the theoretical advances in the theory of electrolytes initiated by Debye that new and profitable fields of inquiry have been opened up; this discussion indicates the advances that have already been made. As is usual with such discussions the occasion was one for stocktaking rather than for startlingly fresh announcements.

The latter half of the volume is taken up with miscellaneous papers on spectroscopy and molecular structure, electrosynthesis, and general physical chemistry.

W. F. K. WYNNE-JONES.

THE DISSOCIATION CONSTANTS OF ACETOACETIC, GLYCOLIC, AND ACETIC ACIDS IN SOLUTIONS OF SODIUM CHLORIDE

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Received February 2, 1934

In the study of the rate of bromination of acetoacetic acid in glycolate and acetate buffer solutions (7) it was necessary to know the ratio between the dissociation constants of acetoacetic acid and, respectively, glycolic and acetic acids. With the object of determining this ratio, solutions of the three acids mixed with their respective sodium salts, with or without sodium chloride, were measured with the quinhydrone electrode against a standard solution of 0.04891 M acetic acid + 0.05024 M sodium acetate. The solutions were prepared in the same way as for the kinetic experiments. As bridge solution 3.5 M potassium chloride was used at 25 and 18°C., while 3.0 M potassium chloride was used at 0°C. The buffer and bridge solution formed a sharp interface in a perpendicular, cylindrical glass tube. Unmack and Guggenheim (9) have found that this is a simple way of obtaining constant, reproducible potentials. In our calculations we have neglected the liquid–liquid potential. This error is probably of no importance when the buffer solutions mentioned above are measured against each other

Before the measurements the platinum electrodes were measured against each other in the same dilute hydrochloric acid. Only electrodes showing a potential difference of less than a few hundredths of a millivolt were used. The reliability of the electrodes during the measurement was tested in the following way. When the E.M.F. was constant (E_1), the electrodes of the two half-cells were interchanged, and the E.M.F. was again measured (E_2). The potential difference between the solutions is $E = \frac{1}{2}(E_1 + E_2)$. $|E_1 - E_2|$ was always less than 0.20 millivolt.

This method could not be used for the acetoacetate buffers. Here the potential was not constant, but decreased at a rate which was proportional to the concentration of sodium acetoacetate and independent of the concentration of acetoacetic acid. The measurements for the solution where the quickest fall was found are given in the diagram. t is the time in minutes from the addition of quinhydrone to the solution. The decrease

may be explained by a reaction between the acetoacetate ion and the quinone. Owing to the linear relationship it is easy to extrapolate to $t = 0$. When the electrodes were interchanged an extra fall of the potential was noticed, as seen from the diagram. For that reason the value of E found by extrapolation of the measurements before the interchange was used. The fall was much slower at 0 than at 18°C.

The acetoacetate buffers contained a small amount of alcohol produced by the hydrolysis of the ester. Some acetate buffers to which was added a little alcohol were measured at 18°C. A decrease of $1.0 \times (C_2H_5OH) \times$

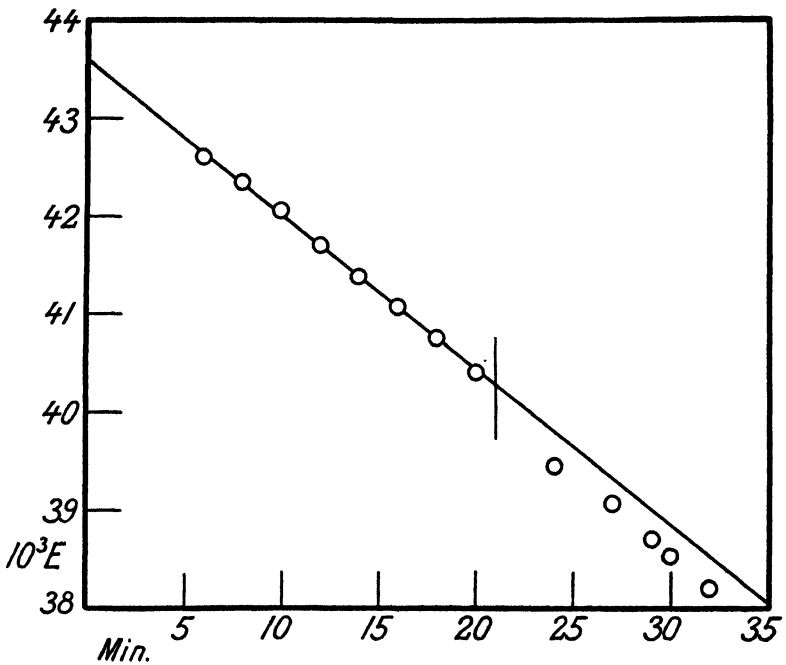

FIG. 1. THE DECREASE OF POTENTIAL IN A SOLUTION OF ACETOACETIC ACID, SODIUM ACETOACETATE, AND QUINHYDRONE

The interchange of electrodes is indicated by the crossing line.

10^{-3} volt was found. This correction was therefore added to the potentials of the acetoacetate buffers both at 18°C. and at 0°C.

The potential, E, of a quinhydrone electrode in a solution with the hydrogen ion activity a_{H^+}, measured against a constant standard electrode, is, when the liquid–liquid potential is neglected, given by the expression

$$\log a_{H^+} = \frac{E}{\rho} + \sigma s - C \tag{1}$$

where

$$\rho = RT/\text{Floge} \tag{2}$$

s is the total salt concentration, and σs the "salt error" of the quinhydrone electrode.

Between the incomplete dissociation constant K_{ac} of a weak acid HB, the dissociation constant K and the same at infinite dilution K^0, we have the following relationship,

$$K_{ac} = a_{H^+}\frac{(B^-)}{(HB)} = K^0\frac{f_{HB}}{f_{B^-}} = Kf_{H^+} \tag{3}$$

where f_{HB}, f_{B^-}, and f_{H^+} are activity coefficients of HB, B^-, and H^+, respectively.

From the equations 1 and 3 we get

$$-\log K_{ac} = C - \frac{E}{\rho} - \sigma s - \log\frac{(B^-)}{(HB)} \tag{4}$$

In a solution of univalent ions we have, according to Debye-Hückel's law,

$$-\log K_{ac} = -\log K^0 - \alpha\sqrt{s} + \beta s \tag{5}$$

α is the same for all the acids HB. β, which is dependent on the nature of the acid, approaches a constant value when $s \rightarrow 0$. Consequently the ratio between K_{ac} for the acid HB and another weak acid HB′ at the same salt concentration is determined by

$$\log\frac{K_{ac}}{K_{ac'}} = \log\frac{K^0}{K^{0\prime}} - (\beta - \beta')s \tag{6}$$

If we assume that f_{H^+} depends only on the total salt concentration, s, and not on the individual nature of B^- and B'^-, we get by means of equation 3

$$\log\frac{K}{K'} = \log\frac{K^0}{K^{0\prime}} - (\beta - \beta')s \tag{7}$$

If we use the abbreviation

$$\varphi \equiv \frac{E}{\rho} + \log\frac{(B^-)}{(HB)} - \alpha\sqrt{s} \tag{8}$$

we get from equations 4 and 5

$$\varphi = C + \log K^0 - (\beta + \sigma)s \tag{9}$$

Hence by means of equation 7

$$\log\frac{K}{K'} = \varphi - \varphi' \tag{10}$$

We calculate K/K' from the experiments by means of equation 10. For each of the solutions we find φ from expression 8. For ρ we use the values, found from equation 2, 0.05418, 0.05774, and 0.05915 at 0, 18, and 25°C., respectively. For α we use the values 0.486, 0.499, and 0.504 at 0, 18, and 25°C., respectively.

The solutions contained usually 0.05 M HB and 0.05 M NaB, to which had been added varying amounts of sodium chloride. Only a few of the solutions contained other concentrations of the acid and its sodium salt. The real concentrations of the undissociated acid HB and its ion B^- were calculated from the stoichiometric concentrations and a rough value of the hydrogen-ion concentration. The results of the measurements at 18°C. are given in table 2. The values of φ calculated from the experiments may be expressed by the formulas in table 1. The next to the last column in table 2 gives δ, the difference between φ found by the measurement and φ calculated from the formulas. It is seen that the linear relationship holds surprisingly well even at high salt concentration. At 0 and 25°C. an equally good agreement was found.

TABLE 1

Value of φ calculated from the experiments

$(0.05 < s < 0.55)$

BUFFER	VALUES OF φ		
	$T = 0$°C.	$T = 18$°C	$T = 25$°C
Acetate	$\varphi = -0.080 - 0.336 \times s$	$\varphi = -0.086 - 0.266 \times s$	$\varphi = -0.089 - 0.240 \times s$
Glycolate	$\varphi = 0.823 - 0.118 \times s$	$\varphi = 0.833 - 0.202 \times s$	
Acetoacetate	$\varphi = 1.100 - 0.246 \times s$	$\varphi = 1.080 - 0.271 \times s$	

By means of equation 10 we now find the following expressions for the ratio L between the dissociation constants:

$$\left.\begin{array}{lll} \text{Acetoacetic acid / Glycolic acid} & 0°\text{C.} & \log L = 0.277 - 0.058 \times s \\ \text{Acetoacetic acid / Glycolic acid} & 18°\text{C.} & \log L = 0.247 - 0.069 \times s \\ \text{Acetoacetic acid / Acetic acid} & 0°\text{C.} & \log L = 1.180 + 0.090 \times s \\ \text{Acetoacetic acid / Acetic acid} & 18°\text{C.} & \log L = 1.166 - 0.005 \times s \end{array}\right\} \quad (11)$$

We have now solved our main problem. In addition we shall find the dissociation constants of the three acids, although with less accuracy than L. If we assume that the linear expressions for φ also hold when $s < 0.05$, we get directly from equation 9 the constants $C + \log K^0$ and $\beta + \sigma$. In order to determine C from equation 1 the solution 0.01009 M hydrochloric acid + 0.0898 M sodium chloride was measured against the standard buffer at 0, 18, and 25°C. According to Bjerrum and Unmack (1) the liquid–liquid potential between this solution and 3.5 M potassium chloride is so small that we may neglect it. For the activity coefficient of the

TABLE 2

Measurements with the quinhydrone electrode in buffer solutions at 18°C.

E for the acetoacetate buffers has been corrected for the effect of the alcohol

BUFFER	(HB) (STOICH.)	(NaB) (STOICH.)	(NaCl)	$E \times 10^3$	$\log \frac{(B^-)}{(HB)}$	s	φ	$\delta \times 10^3$	$-\log K$
Acetate	0.04891	0.05024	0.000	0.00	0.0122	0.050	−0.100	−1	4.598
	0.1489	0.05024	0.000	28.16	−0.4709	0.050	−0.096	+3	4.594
	0.04891	0.05024	0.050	1.86	0.0122	0.100	−0.113	0	4.557
	0.09782	0.1005	0.000	1.20	0.0118	0.100	−0.125	−12	4.568
	0.04891	0.05024	0.149	4.06	0.0122	0.199	−0.140	−1	4.513
	0.04891	0.05024	0.250	5.46	0.0122	0.300	−0.166	0	4.488
	0.04891	0.05024	0.500	7.49	0.0122	0.550	−0.228	+4	4.462
Glycolate	0.04808	0.05000	0.000	52.80	0.0206	0.050	0.822	−1	3.676
	0.1046	0.05000	0.000	72.45	−0.3183	0.050	0.824	+1	3.674
	0.04808	0.05000	0.050	54.86	0.0209	0.100	0.813	0	3.630
	0.04808	0.05000	0.050	54.88	0.0209	0.100	0.814	+1	3.630
	0.04808	0.05000	0.149	57.38	0.0216	0.199	0.793	0	3.580
	0.04808	0.05000	0.250	58.90	0.0216	0.300	0.768	−4	3.553
	0.04808	0.05000	0.500	61.53	0.0218	0.550	0.718	−4	3.516
Aceto-acetate	0.02041	0.02056	0.024	67.12	0.0182	0.045	1.076	+8	3.430
	0.0514	0.0505	0.060	70.27	−0.0008	0.111	1.050	0	3.384
	0.0511	0.0499	0.060	70.47	−0.0034	0.110	1.051	+1	3.384
	0.0511	0.0503	0.060	69.81	0.0000	0.110	1.044	−6	3.392
	0.0769	0.0251	0.085	97.36	−0.4591	0.111	1.061	+11	3.374
	0.0269	0.0749	0.036	43.72	0.4469	0.110	1.039	−11	3.396
	0.0511	0.0498	0.160	72.48	−0.0043	0.210	1.022	−1	3.344
	0.0514	0.0505	0.260	73.48	0.0008	0.311	0.996	0	3.321
	0.0510	0.0499	0.460	75.38	−0.0009	0.510	0.949	+7	3.297

TABLE 3

TEMPERATURE	ACETIC ACID			GLYCOLIC ACID			ACETOACETIC ACID		
	$-\log K^0$	β	$K^0 \times 10^5$	$-\log K^0$	β	$K^0 \times 10^4$	$-\log K^0$	β	$K^0 \times 10^4$
°C.									
0	4.770	0.287	1.70	3.867	0.139	1.36	3.590	0.197	2.57
18	4.748	0.217	1.79	3.829§	0.153	1.48	3.582¶	0.222	2.62
25	4.751†	0.191	1.77	(3.812)*		(1.54)‡			

* The data in parenthesis have been found by extrapolation from 0 and 18°C.

Other determinations:

† MacInnes and Shedlovsky (6), conductivity, 4.756.
Harned and Ehlers (3), concentration cells without liquid junction, 4.756.

‡ Böeseken and Kalshoven (2), conductivity, 1.54×10^{-4}.

§ Larsson and Adell (4), quinhydrone electrode, 3.835.

¶ Widmark (10), hydrogen electrode at about 16°C., 3.55.
Ljunggren (5), kinetic measurements at 25°C., 3.66.

hydrogen ion in sodium chloride solutions ($0.001 < s < 1.5$) Bjerrum and Unmack (1) give the following empirical formulas

$$\left.\begin{array}{ll} 0°C. & -\log f_{H^+} = 0\ 192\ \sqrt{s} - 0\ 207 \times s - 0\ 007 \\ 18°C. & -\log f_{H^+} = 0.166\ \sqrt{s} - 0\ 185 \times s - 0.003 \\ 25°C. & -\log f_{H^+} = 0.161\ \sqrt{s} - 0\ 178 \times s - 0.003 \end{array}\right\} \quad (12)$$

From these formulas we calculate $-\log f_{H^+}$ for the solutions of hydrochloric acid and sodium chloride. For σ we use the value 0.049 (Sörensen, Sörensen, and Linderström-Lang (8)). We find

	At 0°C	*At 18°C.*	*At 25°C*
$E \times 10^3$	142.36	150.43	154.25, 154.18
C	4.690	4.662	4.662

It is now easy to calculate K^0 and β from the constants $C + \log K^0$ and $\beta + \sigma$. The results are given in table 3. In order to find K we use the formulas 3, 4, and 12. $-\log K$ is given in the last column of table 2.

SUMMARY

The ratio between the dissociation constants of acetoacetic acid and, respectively, glycolic and acetic acids was determined by means of the quinhydrone electrode at 0 and 18°C. in solutions of sodium chloride up to 0.5 M.

The dissociation constants at infinite dilution were computed.

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THE VELOCITY OF BROMINATION OF ACETOACETIC ACID

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I. INTRODUCTION

In earlier papers (3, 5) the velocity of bromination of acetoacetic ethyl ester was examined. By this reaction we first get α-monobromoacetoacetic ethyl ester, which reacts with more bromine and gives α,α-dibromoacetoacetic ethyl ester. The velocity of bromination is independent of the concentration of bromine. It is a result of the consecutive enolizations of the acetoacetic and monobromoacetoacetic esters, which reactions are catalyzed by bases in general.

In this paper we examine the velocity of bromination of acetoacetic acid in the following solvents: (1) 0.022 to 0.75 M hydrochloric acid, (2) solutions of acetoacetic acid and sodium acetoacetate, (3) solutions of glycolic acid and sodium glycolate, and (4) solutions of acetic acid and sodium acetate. In the solutions of hydrochloric acid we first get α-monobromoacetoacetic acid, which reacts with more bromine and gives α,α-dibromoacetoacetic acid. In the three other solvents, where the hydrogen-ion concentration is smaller, the substance is brominated only to α-monobromoacetoacetic acid.

It has been found (6) by electrometric measurements that the dissociation constant of acetoacetic acid at keto–enol equilibrium is 2.62×10^{-4} at 18°C. and 2.57×10^{-4} at 0°C. From the kinetic measurements in hydrochloric acid, it follows that the dissociation constant of α-monobromoacetoacetic acid at 0°C. is about 0.021, that is, eighty times as great as that of acetoacetic acid. By comparison with the dissociation constants of propionic, α-bromopropionic, and α,α-dibromopropionic acids at 25°C., which are 1.34×10^{-5}, 1.08×10^{-3}, and 3×10^{-2}, respectively (8)—ratio 1:81:2200—it is estimated that the dissociation constant of α,α-dibromoacetoacetic acid is of the order 0.6. Acetoacetic and monobromoacetoacetic acid can also split off another proton, viz., in the keto forms at the alpha carbon atom and in the enol forms at the enol group. However, this proton is much more firmly bound than that in the carboxyl group. When we speak of the acetoacetate and monobromoacetoacetate ion or of the dissociation of acetoacetic and mono-

bromoacetoacetic acid, we think only of the dissociation at the carboxyl group.

The degree of enolization of acetoacetic acid in dilute hydrochloric acid at 0°C. is, when equilibrium is attained, 0.7 per cent.

In this paper we shall see that the rate of bromination in the solvents mentioned above may be explained on the following assumptions.

(1) The rate of bromination of the enol forms is very great compared with the rate of enolization of the keto forms. The keto forms are not brominated.

(2) Undissociated acetoacetic and monobromoacetoacetic acid are enolized with measurable velocity. The reactions are catalyzed by bases in general.

(3) The rates of enolization of the acetoacetate and monobromoacetoacetate ions are negligible compared with those of the undissociated acids.

In the solutions of hydrochloric acid, acetoacetic acid is practically completely undissociated. The monobromoacetoacetic acid formed by the reaction is, in the more dilute hydrochloric acid, partly dissociated. The course of the reaction in solutions of hydrochloric acid may be explained by the following scheme, which is analogous to scheme 1a-1d (reference 3) for the bromination of acetoacetic ester.

$$CH_3COCH_2COOH \rightarrow CH_3COH{:}CHCOOH \tag{1a}$$

$$CH_3COH{:}CHCOOH + Br_2 \rightarrow (CH_3COCHBrCOOH \rightleftarrows CH_3COCHBrCO_2^- + H^+) + H^+ + Br^- \tag{1b}$$

$$CH_3COCHBrCOOH \rightarrow CH_3COH{:}CBrCOOH \tag{1c}$$

$$CH_3COH{:}CBrCOOH + Br_2 \rightarrow (CH_3COCBr_2COOH \rightleftarrows CH_3COCBr_2CO_2^- + H^+) + H^+ + Br^- \tag{1d}$$

The velocity of bromination is determined by the enolizations of acetoacetic acid (1a) and monobromoacetoacetic acid (1c).

In all the other solvents the acetoacetic acid is incompletely dissociated, while the monobromoacetoacetic acid is practically completely dissociated. Therefore the rate of bromination is here determined only by the enolization of the undissociated part of the acetoacetic acid and the basic catalysis of this reaction.

II. EXPERIMENTAL PROCEDURE

Owing to the instability of acetoacetic acid, only fresh solutions of sodium acetoacetate were used. They were prepared by hydrolysis of acetoacetic ethyl ester during the night before the experiments. The acetoacetic ester was purified through the copper compound (3). To a known amount of the ester in a graduated flask was added a small excess of sodium hydroxide. It was diluted to the mark and placed in a thermostat at 18°C. During the night the ester is completely hydrolyzed.

Goldschmidt and Oslan (1) have found that the velocity of hydrolysis is independent of the excess of sodium hydroxide. At 25°C. they found the unimolecular velocity constant $k_1^* = 0.008$ (min. $^{-1}$). By an asterisk we denote that the velocity constant has been calculated by means of decadic logarithms. Thus $k^* = 0.4343\ k$. In order to find k_1^* at 18°C., we assume that the temperature coefficient is the same as for the methyl ester. For the latter Ljunggren (2) found 2.63 for a temperature increase of 10°C. Hence, we calculate for the ethyl ester $k_1^* = 0.004$ at 18°C. Consequently, after twelve hours at 18°C. only 0.1 per cent of the ester is not hydrolyzed.

The solutions contained the small amount of ethyl alcohol formed by the hydrolysis. By adding suitable amounts of alcohol it was shown that this has no detectable influence on the bromination.

In a solution of acetoacetic acid a slow ketonic decomposition takes place: $CH_3COCH_2COOH \rightarrow CH_3COCH_3 + CO_2$. This reaction has been examined mainly by Widmark (9) and Ljunggren (2). Both the undissociated acid and the ion are decomposed. However the velocity is much greater in acid than in alkaline solution. From experiments of Ljunggren at 37 and 25°C. we calculate the following unimolecular constants for the ketonic decomposition at 18°C.: of the undissociated acetoacetic acid, $k_2^* = 1.61 \times 10^{-4}$ (min.$^{-1}$); of the acetoacetate ion, $k_3^* = 3.6 \times 10^{-6}$ (min.$^{-1}$).

We denote by c_0 the initial concentration of acetoacetic ester, and by c the sum of the concentrations of the ester and the sodium acetoacetate at the time t minutes after the addition of sodium hydroxide. When the hydrolysis is complete, c is the concentration of sodium acetoacetate. The hydrolysis and ketonic decomposition are consecutive unimolecular reactions with the velocity constants at 18°C. $k_1^* = 0.004$ and $k_3^* = 3.6 \times 10^{-6}$, respectively. According to Rakowski (7) we may express the course of such reactions by the equation

$$c = c_0 \left[\frac{k_3}{k_3 - k_1} e^{-k_1 t} - \frac{k_1}{k_3 - k_1} e^{-k_3 t} \right]$$

When the hydrolysis is finished $e^{-k_1 t} = 0$ and consequently

$$c = c_0 \frac{k_1}{k_1 - k_3} e^{-k_3 t}$$

If we introduce the values for k_1^* and k_3^* expressed in hours $^{-1}$, we find that the loss of acetoacetic acid in t hours is $(0.05\ t - 0.1)$ per cent. The concentration, c, of acetoacetate was calculated for each experiment by means of this expression. The solutions were never more than twenty-four hours old when used for the experiments. Consequently less than

1.1 per cent was decomposed. A series of experiments was always carried out within the time of eight hours. During this time the decrease of c is only 0.4 per cent.

The bromination was carried out in the following way. Suitable volumes of water and the slightly alkaline hydrolysis product were measured out and poured into a beaker. To this was added enough potassium bromide solution to make the reacting solution 0.05 M with respect to this substance. This was done in order to repress the hydrolysis of the bromine (reference 5, p. 605). The beaker was placed in a water thermostat at 17.94°C. or in a mixture of ice and water. The solution was stirred vigorously with a mechanical stirrer. When temperature equilibrium was nearly attained, either a solution of hydrochloric acid (in the experiments in hydrochloric acid and in solutions of acetoacetic acid and sodium acetoacetate) or a mixture of glycolic acid and sodium glycolate or of acetic acid and sodium acetate was added from a pipet. After a few minutes, when the solution had attained the temperature for the experiment, the reaction was started by sudden addition of bromine water, usually 25 cc. of 0.1 to 0.2 N, which was already at the temperature of the experiment. In the experiments at 0°C. the temperature rose a little when bromine water was added. 0.03°C. is therefore used as an average value. The bromination was interrupted by sudden addition of an excess of allyl alcohol, mixed with sufficient hydrochloric acid to make the concentration of this acid at least 0.1 N after the experiment. As quickly as possible after the allyl alcohol (2 to 3 seconds), about 1 g. of solid potassium iodide was added. Iodine equivalent with the bromine used by the reaction is slowly liberated. It is titrated with 0.05 N sodium thiosulfate. The solutions from the experiments at 0°C. were slowly heated to 18°C. during the titration.

The alkaline sodium acetoacetate solution was acidified as short a time as possible before the start of the bromination, because the ketonic decomposition is much quicker in acid than in alkaline solution. The time from the addition of acid to the end of the bromination was never more than ten minutes. During this time the decomposition is less than 0.4 per cent at 18°C. and less than 0.1 per cent at 0°C., even when the acidity is so great that all the acetoacetic acid is undissociated. The error thus introduced is negligible. The small amount of acetone formed in the alkaline and acid solution does not interfere with the experiment. Acetone reacts with bromine, although more slowly than acetoacetic acid, but the reaction product does not liberate iodine from potassium iodide. During the titration some of the iodine liberated by the bromination products of acetoacetic acid may react with the acetone in the acid solution, but direct experiments with acetone and iodine in hydrochloric acid have shown that this error is of no importance.

The analytical determination of the bromine used by the reaction caused some difficulties. The method is based on the reactions

$$CH_3COCHBrCOOH + 2I^- + H^+ \rightarrow CH_3COCH_2COOH + Br^- + I_2$$

and

$$CH_3COCBr_2COOH + 4I^- + 2H^+ \rightarrow CH_3COCH_2COOH + 2Br^- + 2I_2$$

It was found necessary to have a rather great concentration of hydrochloric acid during the analysis. If the acidity was too small the iodine was liberated too slowly, and the reaction stopped before an equivalent amount of iodine was set free. In the acetate and glycolate mixtures only a fraction of the iodine was liberated in thirty minutes if no hydrochloric acid was added. From this in connection with the increase in velocity, when the hydrogen-ion concentration is increased, we may conclude that the mono- and di-bromoacetoacetate ions react much more slowly with iodide ions than the undissociated acids. When the solution contained at least 0.1 *N* hydrochloric acid the titration could be successfully finished in ten to fifteen minutes.

Another and much more serious difficulty arose. The results of the titration varied with the time between the additions of allyl alcohol and potassium iodide. In order to study the error, this time was varied in otherwise identical experiments. When the bromination took place in hydrochloric acid of different concentration, a decrease of 1 per cent per 3 seconds was found at 18°C. and of 0.1 to 0.3 per cent at 0°C. When the bromination was carried out in acetate mixtures at 18°C., to which was added together with the allyl alcohol enough hydrochloric acid to make it 0.3 *N*, the decrease in bromine was only 0.1 to 0.2 per cent per 3 seconds. From this we conclude that it is hopeless to do experiments in hydrochloric acid at 18°C., while we may consider the error negligible in hydrochloric acid at 0°C. and in acetate and glycolate buffers at 18 and 0°C., provided that the potassium iodide is added not later than 3 seconds after the allyl alcohol. The decrease in titratable bromine is probably caused by a transformation (possibly a ketonic decomposition) of mono- and di-bromoacetoacetic acid into substances which do not react with potassium iodide. The rather slow decrease of titratable bromine in acetate mixtures, where the reaction product is monobromoacetoacetic acid, seems to show that this acid is transformed much more slowly than dibromoacetoacetic acid. Probably the transformation takes place also during the bromination as well as after potassium iodide is added. Although the time of bromination is always very short, and the reaction with potassium iodide rather quick, it is not quite excluded that the error can have some importance. However, the results given later in the paper

seem to show that the reaction products are not transformed to any essential degree during the part of the reaction which is used for the calculations.

III. BROMINATION OF ACETOACETIC ACID IN HYDROCHLORIC ACID

Experiments were carried out at 0.03°C. in 0.022 to 0.75 N hydrochloric acid. We shall see that the results agree with the explanation given in the introduction (scheme 1a-1d). According to this the rate of bromination is determined by the consecutive enolizations of the undissociated acetoacetic and monobromoacetoacetic acid (unimolecular constants k_0 and h_0, respectively). The acetoacetic acid (dissociation constant 2.57×10^{-4}) may be considered completely undissociated in all the solutions of hydrochloric acid. At a given concentration of hydrochloric acid a fraction γ' of the monobromoacetoacetic acid is undissociated. If we use the abbreviation $\gamma' h_0/k_0 \equiv r$, and denote by ϵ the degree of enolization of the acetoacetic acid at keto–enol equilibrium, we get for the course of the bromination the following expression, which is analogous to the one found for acetoacetic ester (reference 3, formula 13),

$$\frac{c - \frac{x}{4}}{c} = A\, 10^{-k_0 * t} - \left(A - 1 + \frac{\epsilon}{2}\right) 10^{-r k_0 * t} \tag{3}$$

where c is the initial concentration of acetoacetic acid, x the bromine used by the reaction t minutes after its start in equivalents per liter, and

$$A \equiv (1 - \epsilon)\left(1 + \frac{1}{2(r - 1)}\right)$$

It was first shown that the velocity is independent of the concentration of bromine. Hence, the reactions by which bromine is taken up are very rapid compared with those which determine the velocity. It was also shown that $\left(c - \frac{x}{4}\right) \Big/ c$, when t is constant, is independent of the initial concentration of acetoacetic acid. Consequently, the reactions which determine the velocity follow the unimolecular law.

The agreement with formula 3 was shown in a similar way as with acetoacetic ester (3). First ϵ is determined. In another paper (3) it was shown that formula 3 of the present paper, when t is small, may be written

$$\left(c - \frac{x}{4}\right) \Big/ c = 1 - \frac{\epsilon}{2} - t\,\frac{k_0}{2}\,[1 + (r - 1)\epsilon]$$

ϵ is small, and r is in the experiments on acetoacetic acid not much different from 1. Hence we have with good approximation, when t is small,

$$\left(c - \frac{x}{4}\right) \Big/ c = 1 - \frac{\epsilon}{2} - \frac{k_0}{2}\,t \tag{4}$$

In figure 1 $\left(c - \frac{x}{4}\right) \Big/ c$ is plotted against t for all the experiments in solutions of hydrochloric acid, for which $t < 0.2$ min. We shall see later that the mean value of k_0^* for all the solutions of hydrochloric acid is 0.235, which corresponds to $\frac{k_0}{2} = 0.271$. All the points in figure 1 fall close to the straight line with the slope -0.271. If we extrapolate to $t = 0$, we find $\epsilon = 0.0073$.

r is here not much different from 1. It is therefore very difficult to find the values of k_0^* and r which at a given hydrochloric acid concentration give the best agreement between formula 3 and the experiments. We must use the very time-wasting method described previously (reference

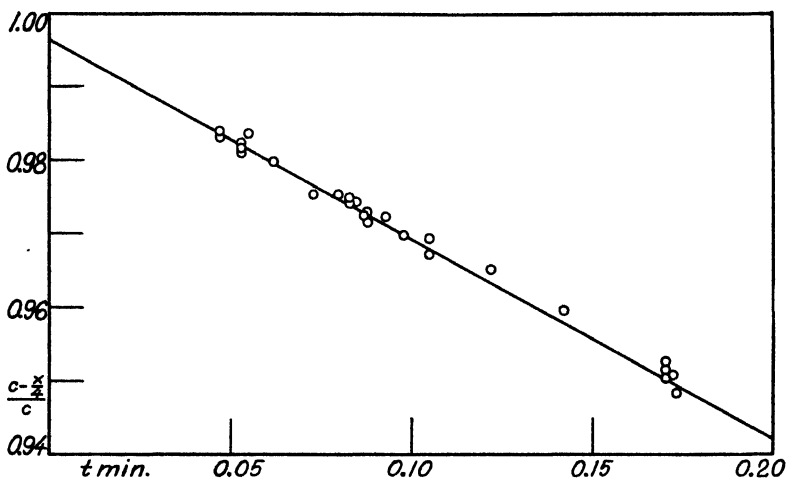

FIG. 1. BROMINATION OF ACETOACETIC ACID IN HYDROCHLORIC ACID

3, pp. 754–5). For each pair of values of x and t found by experiment and for a series of values of r we calculate by the method of trial and error the values of k_0^* which satisfy formula 3. In this way we find the values of r for which the variation of k_0^* is smallest. As seen from formula 4, k_0^* is independent of r when t is small. However, we can not determine k_0^* with sufficient accuracy from these experiments. For the determination of k_0^* and r we only use experiments in which $0.94 > \left(c - \frac{x}{4}\right) \Big/ c > 0.5$ (values of k_0^* printed in italics in table 1). Toward the end of the reaction, when $\left(c - \frac{x}{4}\right) \Big/ c < 0.5$, we get a considerable decrease in the value of k_0^*. We always disregard such experiments. The same decrease was found in experiments on acetoacetic ester (3, 5). It may be explained by a consecutive reaction.

Table 1 contains the experimental results and the calculation of k_0^* and r for a series of experiments in hydrochloric acid. In the eighth column are given the values of $\frac{x}{4}$ calculated from formula 3 when we use the constants given at the top of the table. δ, the difference between $\frac{x}{4}$ found by experiment and calculated from formula 3, is given in the last column. The average deviation $\delta_m = \sqrt{\frac{\Sigma\delta^2}{n-1}}$ where n is the number of experiments, is 2.9×10^{-6}.

TABLE 1

Bromination of acetoacetic acid in (0.0220 M hydrochloric acid + 0.050 M potassium bromide) at 0.03°C.

$\epsilon = 0.0073$; $k_0^* = 0.230$; $r = 0.61$

	$c \times 10^3$	$\frac{x}{4} \times 10^3$	$\frac{c - \frac{x}{4}}{c}$	k_0^* (r = 0 50)	k_0^* (r = 0 61)	k_0^* (r = 0 70)	$\frac{x}{4} \times 10^3$ (CALCD)	$\delta \times 10^6$
minutes								
0.047	3 201	0 051	0.9840	0.230	0.230	0.230	0.051	0
0.083	3.209	0.080	0.9750		0.227		0.081	−1
0.122	3.200	0.111	0.9652	0.227	0.226	0.225	0.113	−2
0.170	3.207	0.152	0.9526		0.229		0 153	−1
0.250	2.798	0.189	0.9324	0.231	*0.229*	0.227	0.190	−1
0.670	2 795	0.470	0.8318	0.234	*0.230*	0.226	0 470	0
1.003	2.801	0.681	0.7568	0.238	*0.232*	0.227	0.676	+5
1.503	2.794	0 948	0 6605	0.238	*0.229*	0.223	0.953	−5
2 000	2 799	1.201	0.5710		*0.230*	0.223	1.198	+3
2.337	2.793	1.329	0 5241	0.239	0 227	0.218	1.344	(−15)
3.000	2.796	1 563	0.4410	0.234	0 222		1.602	(−39)
δ_m ..								2.9×10^{-6}

Table 2 gives a summary of eleven series of experiments in hydrochloric acid of different concentrations. The initial hydrogen-ion concentration $(H^+)_0$ is given in the first column. The third column contains the total salt concentration, s. The constants, k_0^* and r, found from the experimental results are given in the fourth and fifth columns. The last column gives the average deviation δ_m, and the last but one the number of experiments, n, used for its calculation. The mean value of δ_m for all the series is 3.3×10^{-6}. The volume during the reaction being 200 cc., this corresponds to 0.05 cc. of 0.05 N thiosulfate. In all the solutions the reaction may be expressed by formula 3 with an accuracy corresponding to the experimental error. The total unsystematic part of the experimental error thus corresponds to an average error of 0.05 cc. on the titration.

The values of k_0^* found for the different solutions of hydrochloric acid are sufficiently constant when we consider the rather small accuracy in the computation of k_0^* and r. The mean value of k_0^* is 0.235. r increases with increasing concentration of hydrochloric acid and attains a constant value 1.15 in the most concentrated solutions. If, as suggested by the explanation given above, only the undissociated part γ' of the monobromoacetoacetic acid is brominated, we find γ' for each of the solutions by dividing r by the constant value of r at great acid concentration. γ' calculated in this way is given in the sixth column of table 2.

According to scheme 1 hydrogen ions are formed by the reaction. In the second column of table 2 is given $(H^+)_m$, a mean value of the hydrogen-ion concentration. If the explanation holds $\frac{1-\gamma'}{\gamma'}(H^+)_m$ is the dissociation

TABLE 2

Bromination of acetoacetic acid in hydrochloric acid at 0.03°C.

KBr, 0.050 *M*. NaCl, 0.004 *M* (except in the series marked †, which contains NaCl, 0 304 *M*)

$(H^+)_0$	$(H^+)_m$	s	k_0^*	r	γ'	K	n	$\delta_m \times 10^6$
0.0220	0.0238	0 074	0.230	0 61	0.53	0 021	9	2.9
0 0260	0 0280	0 078	0.234	0.69	0.60	0.019	9	3.0
0 0337	0.0357	0.086	0.238	0.71	0.62	0.022	8	4 3
†0.0337	0 0356	0.386	0.226	0.66	0 57	(0.027)	9	4 1
0.0459	0.0480	0 098	0.239	0.80	0 70	0.021	8	3 5
0.0966	0 0986	0.149	0.240	0.92	0.80	0.025	8	2.3
0.120	0.122	0.172	0.240	1 00	0 87	0.018	11	2.9
0 247	0 249	0.300	0.240	1.06	0.92	0.022	7	4 0
0.37	0.37	0.42	0.238	1.10	0.96	0 02	11	2 9
0.50	0 50	0.55	0 234	1 15	1.00		7	3 2
0.75	0 75	0 80	0.228	1.15	1.00		7	3 0

Mean values: $k_0^* = 0.235$, $h_0^* = 0.27$, $K = 0.021$, $\delta_m = 3.3 \times 10^{-6}$.

constant, K, of monobromoacetoacetic acid. K is given in the seventh column of table 2. Although the values of r are only rough, and the salt concentration, s, varies from 0.074 to 0.80, K is nearly constant. The average value is 0.021, eighty times as great as the dissociation constant of acetoacetic acid. This value is reasonable as seen from the following comparison. The ratio between the dissociation constants of monobromoacetic and acetic acids at 25°C. is $1.38 \times 10^{-3}/1.77 \times 10^{-5} = 77:1$, and that between the constants for α-monobromopropionic and propionic acids is $1.08 \times 10^{-3}/1.34 \times 10^{-5} = 81:1$.

$r = 1.15$, when $\gamma' = 1$. Hence the velocity constant for the enolization of undissociated monobromoacetoacetic acid at 0°C. is $h_0^* = 1.15 \times 0.235 = 0.27$.

IV. BROMINATION OF SOLUTIONS OF ACETOACETIC ACID AND SODIUM ACETOACETATE

In this chapter the rate of bromination was studied at 0 and 18°C. in solutions containing both acetoacetic acid and sodium acetoacetate. According to the explanation given before, the rate is determined by the enolizations of the undissociated forms of acetoacetic and monobromoacetoacetic acids, which reactions are catalyzed by bases. In the preceding chapter it was found that the velocity constants for the enolizations of the two acids, when no catalyst is added, are of the same order of magnitude. This probably also holds for the catalyzed reactions. In the acetoacetic acid–sodium acetoacetate mixtures the hydrogen-ion concentration is so small that the monobromoacetoacetic acid is practically completely dissociated. Consequently, this is not further brominated during the experiment. The velocity is determined only by the enolization of undissociated acetoacetic acid, which proceeds by two simultaneous reactions, the "uncatalyzed" water reaction with the velocity constant k_0 and the reaction catalyzed by the acetoacetate ion (catalytic constant k_{R^-}). Hence, we may express the velocity by the differential equation

$$\frac{d\frac{x}{2}}{dt} = k_0(HR) + k_{R^-}(R^-)(HR) \tag{6}$$

According to scheme 1b hydrogen ions are produced by the bromination. The gross reaction is

$$CH_3COCH_2COOH + Br_2 + 2CH_3COCH_2CO_2^- \rightarrow CH_3COCHBrCO_2^- + Br^- + 2CH_3COCH_2COOH$$

or

$$2CH_3COCH_2CO_2^- + Br_2 \rightarrow CH_3COCHBrCO_2^- + CH_3COCH_2COOH + Br^- \tag{7}$$

It is the object of the following examination to show that the velocity of bromination agrees with equation 6 and scheme 7. In addition, we shall determine the constants k_0 and k_{R^-}. Thus, k_0 is here found independently of the determination in the last chapter.

The initial stoichiometric concentrations of acetoacetic acid and sodium acetoacetate are denoted by $c - b$ and b, respectively. At the start of the bromination we have $(HR) = c - b - (H^+)$ and $(R^-) = b + (H^+)$. According to scheme 7 we have at the time t

$$(HR) = c - b + \frac{x}{2} - (H^+) \tag{8}$$

$$(R^-) = b - x + (H^+) \tag{9}$$

(H^+) increases considerably during the reaction.

In each experiment within a series we have determined a pair of values of x and t. We first calculate (H^+) corresponding to each value of x in the series by means of expressions 8 and 9 and

$$(H^+) = \frac{(HR)}{(R^-)} K_{HR} \tag{10}$$

For the dissociation constant K_{HR} of acetoacetic acid we use the values which have been determined electrometrically at 0 and 18°C. in solutions of sodium chloride (6).

We now know for each experiment in the series values of x, (HR), (R^-), and t. The object is to determine such values of k_0 and k_{R^-} that equation 6 is satisfied for all the experiments. By numerical integration of the curves which we obtain by plotting (HR) and the product $(HR)(R^-)$ against t, we find values of the integrals

$$I_0 \equiv \int_{t_1}^{t} (HR)\, dt \quad \text{and} \quad I_{R^-} \equiv \int_{t_1}^{t} (HR)(R^-)\, dt \tag{12}$$

We denote by $\Delta\left(\frac{x}{2}\right)$, ΔI_0, and ΔI_{R^-} the increases of $\frac{x}{2}$, I_0, and I_{R^-} when going from the mth to the nth experiment in a series. Hence, equation 6 may be written

$$\Delta\left(\frac{x}{2}\right) = k_0 \Delta I_0 + k_{R^-} \Delta I_{R^-} \tag{14}$$

or

$$\frac{\Delta\left(\frac{x}{2}\right)}{\Delta I_{R^-}} = k_{R^-} + k_0 \frac{\Delta I_0}{\Delta I_{R^-}} \tag{15}$$

The change of $\frac{\Delta I_0}{\Delta I_{R^-}}$ when going from one pair of experiments to another within a series, is so small that we cannot get a good determination of k_0 and k_{R^-} from a single series without knowing one of them. However we can get this by combining all the series at a certain temperature. In the different series we have mainly varied the concentration c. In the experiments with the smallest c, the catalytic reaction plays a subordinate part. Here $k_{R^-}\Delta I_{R^-}$ is small compared with $k_0 \Delta I_0$. In the experiments with the greatest c, the catalytic reaction is of especially great importance. Here $k_{R^-}\Delta I_{R^-} > k_0 \Delta I_0$. When we compute one pair of values of k_0 and k_{R^-} from all the experiments at constant temperature, we must naturally assume that the constants are the same in all the solvents used. The salt concentration only varies from 0.056 to 0.087 M. It is consequently

excluded that the change in primary salt effect can be important. Equations 15 are solved graphically by plotting $\Delta\left(\frac{x}{2}\right) \Big/ \Delta I_{R^-}$ against $\Delta I_0/\Delta I_{R^-}$ for all the experiments (figure 2). Although the velocity, especially at

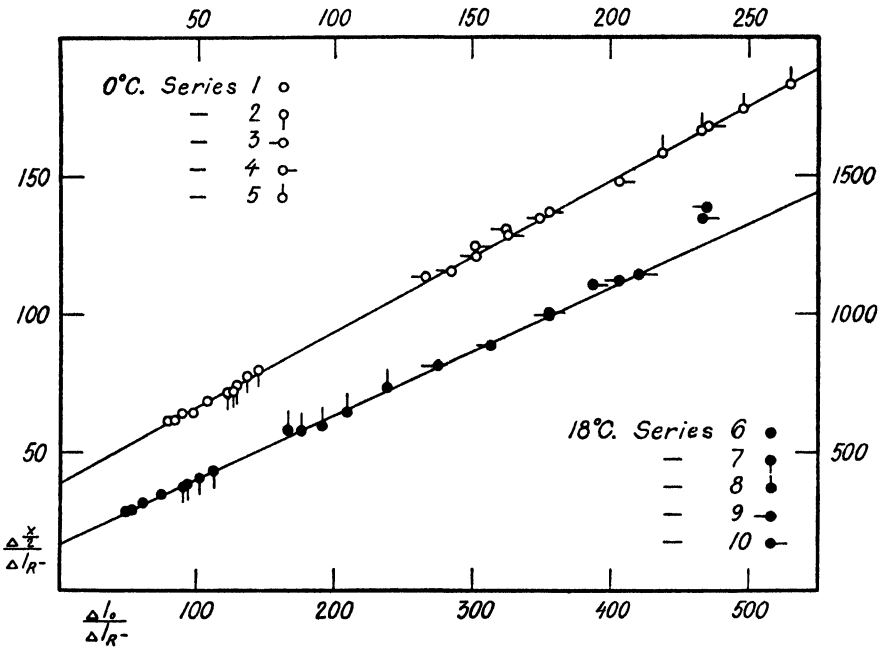

FIG. 2. BROMINATION OF SOLUTIONS OF ACETOACETIC ACID AND SODIUM ACETOACETATE

Coördinates at the top and to the left are for the experiments at 0°C.; those at the bottom and to the right are for the experiments at 18°C.

18°C., is so great that it is difficult to follow the reaction, the points fall close along straight lines, which determine the constants k_0 and k_{R^-}. We find

t	k_0	k_{R^-}	k_0^*	$k_{R^-}^*$
degrees C.				
0.03	0.544	38.8	0.236	16.9
17.94	2.30	172	0.999	74.7

In table 3 is given the composition of the solutions in ten series of experiments, five at each temperature. Table 4 gives the experimental data for series 1. In order to test how well the experiments agree with equation 14 when the values of k_0 and k_{R^-} are introduced, we calculate from this

TABLE 3

Bromination of solutions of acetoacetic acid and sodium acetoacetate

All the solutions contained KBr, 0.050 *M*

TEMPERATURE	SERIES	$b \times 10^3$	$c \times 10^3$	(NaCl)	s	$K_{HR} \times 10^4$	k_0	k_{R^-}
degrees C.								
0.03	1	29.06	33.63	0.008	0.087	4.0	0.544	38.8
	2	17.81	19.84	0 004	0.072	3.9		
	3	8.57	10.48	0.003	0.062	3.8		
	4	7.508	8.515	0.002	0.059	3.8		
	5	4.882	5.373	0.001	0.056	3.7		
17.94	6	26 43	29.45	0.006	0.082	4.0	2.30	172
	7	13.65	14.89	0 003	0.067	3.9		
	8	7 283	8.300	0.002	0.059	3.8		
	9	4 629	5.298	0.001	0.056	3.8		
	10	3 778	4.554	0.002	0.056	3.8		

TABLE 4

Bromination of solutions of acetoacetic acid and sodium acetoacetate at 0.03°C.

Series 1

NO.	t	$\frac{x}{2} \times 10^3$ (EXPTL.)	$\frac{x}{2} \times 10^3$ (CALCD.)	$\delta \times 10^3$	$(H^+) \times 10^3$	$(HR) \times 10^3$	$(R^-) \times 10^3$	$(HR)(R^-) \times 10^6$	$I_0 \times 10^3$	$I_{R^-} \times 10^6$
	minutes									
1	0.062	0.61	0.63	−0.02	0.07	5.14	27.91	143 5	0.000	0.00
2	0.100	0.96	0.95	+0.01	0.08	5.50	27.22	149.7	0.202	5.57
3	0.168	1.58	1.58	0.00	0.09	6.10	25.99	158 5	0 597	16.05
4	0.255	2.45	2.44	+0.01	0.11	6.92	24 27	167.9	1.163	30.27
5	0.333	3.28	3.27	+0.01	0.14	7.72	22.64	174.8	1.734	43.65
6	0.425	4.31	4.31	0.00	0.17	8.71	20.61	179.5	2.490	59.98
7	0.503	5 29	5.25	+0.04	0.21	9.68	18.69	180 9	3.207	74.06
8	0.583	6.18	6.25	−0.07	0.25	10.49	16.95	177.8	4.014	88.44
9	0.667	7.35	7.32	+0.03	0.32	11.57	14.68	169.8	4.940	103.05

NO.	$\Delta\left(\frac{x}{2}\right) \times 10^3$	$\Delta I_0 \times 10^3$	$\Delta I_{R^-} \times 10^6$	$\frac{\Delta\left(\frac{x}{2}\right)}{\Delta I_{R^-}}$	$\frac{\Delta I_0}{\Delta I_{R^-}}$
5–1	2.67	1.734	43.65	61.2	39.7
6–2	3.35	2.288	54.41	61.6	42.1
7–3	3.71	2.610	58.01	64.0	45.0
8–4	3.73	2.851	58.17	64.1	49.0
9–5	4.07	3.206	59.40	68.5	54.0

equation $\Delta\left(\frac{x}{2}\right)$, when going from the first to each of the other experiments in the series. In order to calculate $\frac{x}{2}$ we might assume that experiment No. 1 has no error, but it is more reasonable to calculate $\frac{x}{2}$ from the assump-

TABLE 5

Bromination of solutions of acetoacetic acid and sodium acetoacetate

Series 2 to 10

SERIES	t	$\frac{x}{2} \times 10^3$ (EXPTL.)	$\delta \times 10^3$	SERIES	t	$\frac{x}{2} \times 10^3$ (EXPTL.)	$\delta \times 10^3$	SERIES	t	$\frac{x}{2} \times 10^3$ (EXPTL.)	$\delta \times 10^3$
	minutes				*minutes*				*minutes*		
2	0.047	0.234	+0.006	5	0.058	0.039	−0.002	8	0.057	0.295	−0.037
	0.105	0.404	+0.014		0.307	0.139	0.000		0.087	0.469	0.000
	0.205	0.681	−0.010		0.500	0.227	+0.001		0.120	0.664	+0.029
	0.307	1.005	−0.021		0.697	0.324	−0.002		0.155	0.837	+0.011
	0.403	1.366	−0.004		0.997	0.502	0.000		0.190	1.029	−0.007
	0.503	1.747	−0.013		1.258	0.682	+0.003		0.223	1.245	−0.001
	0.608	2.173	−0.007		1.500	0.863	−0.003		0.270	1.572	0.000
	0.703	2.613	+0.006						0.307	1.841	−0.008
	0.803	3.113	+0.026						0.360	2.283	+0.011
3	0.053	0.138	−0.007	6	0.043	1.16	−0.06	9	0.053	0.157	−0.011
	0.205	0.426	+0.006		0.073	2.11	+0.03		0.142	0.403	+0.001
	0.310	0.615	−0.010		0.092	2.65	−0.04		0.205	0.593	−0.005
	0.407	0.811	−0.013		0.137	4.28	−0.03		0.257	0.787	+0.005
	0.503	1.041	+0.008		0.168	5.61	+0.06		0.297	0.937	+0.002
	0.608	1.273	−0.001		0.208	7.28	+0.01		0.357	1.181	−0.006
	0.705	1.495	−0.012		0.240	8.72	+0.05		0.407	1.412	−0.001
	0.807	1.777	+0.013						0.453	1.649	+0.014
	0.900	2.019	+0.013						0.497	1.952	(+0.095)
4	0.060	0.081	−0.015	7	0.047	0.403	−0.001	10	0.107	0.313	−0.011
	0.202	0.226	0.000		0.057	0.479	+0.001		0.150	0.446	−0.004
	0.320	0.341	−0.004		0.108	0.908	+0.006		0.185	0.566	+0.004
	0.500	0.537	−0.006		0.150	1.336	+0.022		0.223	0.670	−0.021
	0.753	0.869	+0.007		0.227	2.180	−0.033		0.257	0.811	−0.003
	1.000	1.229	+0.007		0.253	2.537	−0.023		0.290	0.954	+0.014
	1.250	1.638	+0.004		0.287	3.052	+0.006		0.320	1.063	+0.004
	1.505	2.094	−0.006		0.320	3.577	+0.025		0.353	1.213	+0.018
	1.747	2.595	+0.014								

tion that the algebraic sum of the errors is as near 0 as possible. The values in the fourth column of table 4 have been found in this way. The fifth column gives δ, the difference between the experimental and calculated value of $\frac{x}{2}$. It is seen that the agreement is good.

In table 5 is given a short survey of the nine other series of experiments.

In the last chapter we found $k_0^* = 0.235$, which is a mean value of eleven series of experiments on the bromination of acetoacetic acid in solutions of hydrochloric acid at 0°C. This is in good agreement with the value $k_0^* = 0.236$ found in this chapter. It may be mentioned that the calculation of the experiments in hydrochloric acid was completed before the calculation of the experiments in this chapter.

V. BROMINATION OF ACETOACETIC ACID IN GLYCOLATE AND ACETATE BUFFER SOLUTIONS

The hydrogen-ion concentration of the solutions used in this chapter is so small that only a rather small part of the acetoacetic acid is undissociated, and the monobromoacetoacetic acid formed by the bromination is completely dissociated. In agreement with the explanation given in the introduction, the velocity of bromination is determined only by the enolization of the undissociated acetoacetic acid, which reaction is catalyzed by bases. The reaction product, monobromoacetoacetic acid, is not further brominated. If the solution contains the weak acid HB and its sodium salt NaB, the velocity is determined by the differential equation

$$\frac{d\left(\frac{x}{2}\right)}{dt} = k_0(\mathrm{HR}) + k_{\mathrm{R}^-}(\mathrm{R}^-)(\mathrm{HR}) + k_{\mathrm{B}^-}(\mathrm{B}^-)(\mathrm{HR}) \tag{16}$$

where k_{B^-} is the catalytic constant for the base B^-.

By the bromination of one molecule of acetoacetic acid to the monobromoacetoacetate ion, two hydrogen ions are set free

$$\mathrm{CH_3COCH_2COOH} + \mathrm{Br_2} \rightarrow \mathrm{CH_3COCHBrCO_2^-} + \mathrm{Br^-} + 2\mathrm{H^+} \tag{17}$$

We shall see that the experiments in glycolate and acetate buffer solutions at 0 and 18°C. agree with equation 16 and scheme 17. In addition, we shall determine the catalytic constants of glycolate and acetate ions.

The buffer solutions were prepared from glycolic or acetic acid and sodium hydroxide as previously described (5). The volume during the bromination was always 200 cc. We use the following notations for the stoichiometric concentrations. c is the total concentration of undissociated and dissociated acetoacetic acid at the beginning of the experiment. $c = (\mathrm{HR}) + (\mathrm{R}^-)$, when $t = 0$. g is the total concentration of the acid HB and its salt NaB. $g = (\mathrm{HB}) + (\mathrm{B}^-)$. b is the total concentration (referred to the volume during the bromination) of the sodium hydroxide used for the preparation of the amount of buffer solution and alkaline sodium acetoacetate solution taken for the experiment. $b = (\mathrm{R}^-) + (\mathrm{B}^-) - (\mathrm{H}^+)$, when $t = 0$.

At the time t we have

$$(\mathrm{HR}) + (\mathrm{R}^-) = c - \frac{x}{2} \tag{18}$$

and

$$(\mathrm{HB}) + (\mathrm{B}^-) = g \tag{19}$$

$$(\mathrm{R}^-) + (\mathrm{B}^-) - (\mathrm{H}^+) = b - x \tag{20}$$

We denote by γ_0, γ, and γ_∞ the fractions of the acetoacetic acid which are undissociated at the times 0, t, and ∞, respectively. We use the abbreviation

$$\gamma_m \equiv \tfrac{1}{2}(\gamma_0 + \gamma_\infty) \tag{21}$$

From equations 18 to 20 and

$$(\mathrm{HR}) = \gamma\left(c - \frac{x}{2}\right) \tag{22}$$

we get

$$(\mathrm{R}^-) = (1 - \gamma)\left(c - \frac{x}{2}\right) \tag{23}$$

$$(\mathrm{HB}) = g - b - (\mathrm{H}^+) + c(1 - \gamma) + \frac{x}{2}(1 + \gamma) \tag{24}$$

and

$$(\mathrm{B}^-) = b + (\mathrm{H}^+) - c(1 - \gamma) - \frac{x}{2}(1 + \gamma) \tag{25}$$

If we denote by L the ratio between the dissociation constants of acetoacetic acid and the acid HB

$$L \equiv K_{\mathrm{HR}}/K_{\mathrm{HB}} \tag{26}$$

we have

$$\gamma = \frac{(\mathrm{HB})}{L(\mathrm{B}^-) + (\mathrm{HB})}$$

By introducing equations 24 and 25 we obtain

$$\gamma = \frac{g - b - (\mathrm{H}^+) + c(1 - \gamma) + \frac{x}{2}(1 + \gamma)}{g + (L - 1)\left[b + (\mathrm{H}^+) - c(1 - \gamma) - \frac{x}{2}(1 + \gamma)\right]} \tag{27}$$

$$\gamma_0 = \frac{g - b - (\mathrm{H}^+) + 2c - (1 + \gamma_0)c}{g + (L - 1)(b + (\mathrm{H}^+) - 2c) + (L - 1)(1 + \gamma_0)c} \tag{28}$$

and

$$\gamma_\infty = \frac{g - b - (\mathrm{H}^+) + 2c}{g + (L - 1)(b + (\mathrm{H}^+) - 2c)} \tag{29}$$

The hydrogen-ion concentration increases so little during the bromination that it is sufficiently accurate to use an average value calculated from the expression

$$(H^+) = K_{HR} \frac{\gamma_m}{1 - \gamma_m} \tag{30}$$

In order to calculate γ_0, γ_∞, γ_m, and (H^+) from the expressions 28, 29, 21, and 30, we proceed in the following way. We first calculate approximate values of γ_0 and γ_∞ by setting $(H^+) = 0$ and $\gamma_0 = 0$ on the right side of equations 28 and 29. In another paper (6) L has been determined electrometrically in solutions of varying salt concentration, s. By means of equation 21 we now find a preliminary value of γ_m, which we introduce into equation 30. In this way we get a sufficiently good value of (H^+). γ_∞ is now calculated from equation 29. By introducing the preliminary value of γ_0 on the right side of equation 28 we find a better value of γ_0, and continue in the same way until a repetition gives the same value. From the final values of γ_0 and γ_∞ we calculate the mean value γ_m.

If we use the abbreviations

$$f_0 \equiv \frac{k_0}{k_{B^-}} \quad \text{and} \quad f_R \equiv \frac{k_{R^-}}{k_{B^-}} \tag{31}$$

the differential equation 16 may be written in the following way

$$\frac{d\left(\frac{x}{2}\right)}{dt} = k_{B^-}(HR)\left[f_0 + f_{R^-}(R^-) + (B^-)\right] \tag{32}$$

If we introduce equations 22, 23, and 25, we get

$$\frac{d\left(\frac{x}{2}\right)}{dt} = k_{B^-}\gamma\left(c - \frac{x}{2}\right)\left[f_0 + b + (H^+) - (1 - f_{R^-})(1 - \gamma)c - (1 + \gamma + (1 - \gamma)f_R)\frac{x}{2}\right] \tag{33}$$

For the first γ in this equation we introduce expression 27. In the equation thus obtained we use for γ the approximate value γ_m. We use the abbreviations

$$E \equiv \frac{g - b - (H^+) + 2c}{1 + \gamma_m} - c \tag{34}$$

$$F \equiv \frac{b + (H^+) + f_0 - (1 - f_{R^-})(1 - \gamma_m)c}{(1 + \gamma_m) + (1 - \gamma_m)f_{R^-}} \tag{35}$$

$$G \equiv \frac{g + (L - 1)(b + (H^+) - (1 - \gamma_m)c)}{(L - 1)(1 + \gamma_m)} \tag{36}$$

The differential equation 33 may now be written

$$\frac{d\left(\frac{x}{2}\right)}{dt} = k_{B^-} \frac{1 + \gamma_m + (1 - \gamma_m) f_{R^-}}{L - 1} \frac{\left(c - \frac{x}{2}\right)\left(E + \frac{x}{2}\right)\left(F - \frac{x}{2}\right)}{\left(G - \frac{x}{2}\right)} \tag{37}$$

We integrate equation 37 and introduce $\frac{x}{2} = c(\gamma_0\epsilon + (1 - \gamma_0)\epsilon_i)$, when $t = 0$, where ϵ and ϵ_i are the degrees of enolization at keto–enol equilibrium of undissociated acetoacetic acid and the acetoacetate ion respectively. $c(\gamma_0\epsilon + (1 - \gamma_0)\epsilon_i)$ is negligible compared with E and F. We thus get

$$S + k^*t = f(x) \tag{38}$$

where we have used the following abbreviations

$$f(x) \equiv \log \frac{c}{c - \frac{x}{2}} + \Delta_1 - \Delta_2 \tag{39}$$

$$\Delta_1 \equiv M \log \frac{E + \frac{x}{2}}{E} \tag{40}$$

$$\Delta_2 \equiv N \log \frac{F}{F - \frac{x}{2}} \tag{41}$$

$$k \equiv \gamma_\infty [k_0 + k_{B^-}(B^-)_{t\to\infty}] \tag{42}$$

$$M \equiv P \frac{g(b + (H^+) - 2c + f_0)}{g + (L - 1)(b + (H^+) - 2c)} \tag{43}$$

$$N \equiv (1 - f_0 P)\gamma_\infty \tag{44}$$

$$P \equiv \frac{(1 + \gamma_m)L}{(1 + \gamma_m)(g + f_0) + (1 - \gamma_m) f_{R^-}(g - b - (H^+) + 2c)} \tag{45}$$

$$S \equiv -\log(1 - \gamma_0\epsilon - (1 - \gamma_0)\epsilon_i) \tag{46}$$

In order to show that the experiments agree with formula 38, we proceed in the following way. The composition of the solution within a series of experiments is given by g, b, c, and the total salt concentration s. We first calculate L from formulas 11 (reference 6). We then calculate γ_0, γ_∞, γ_m, and (H^+) from expressions 28, 29, 21, and 30 as explained before. Δ_1 and Δ_2 in formula 39 are rather small compared with $\log \frac{c}{c - \frac{x}{2}}$. We may

therefore find an approximate value of k^* from the slope of the straight line which we get by plotting $\log \frac{c}{c - \frac{x}{2}}$ against t. When we use the values of k_0^* and $k_{R^-}^*$ found in the last chapter and the rough value of k^* found here, we calculate by means of expressions 42 and 31 approximate values of f_0 and f_{R^-}. From these values we calculate by means of expressions 34 to 36, 39 to 41, and 43 to 45 approximate values of $f(x)$, which we plot against t. In this way we find a better value of k^*. We repeat the computation, and continue until a repetition gives the same value of k^*. We now find $k_{B^-}^*$ from equation 42. S is the intercept on the ordinate axis of the straight line we get by plotting $f(x)$ against t.

TABLE 6

Bromination of acetoacetic acid in a mixture of glycolic acid and sodium glycolate at 0.03°C.

g = 0.09285	b = 0 07802	c = 0.003084	(KBr) = 0.050
(C_2H_5OH) = 0.0031	s = 0.128	L = 1.862	(H^+) = 0.00006
γ_∞ = 0.1353	γ_0 = 0 1110	γ_m = 0.1232	f_0 = 0 0124
f_{R^-} = 0 89	E = 0.01557	F = 0 04737	M = 0 787
N = 0.115	k^* = 0.2211	$k_{B^-}^*$ = 19.4	S = 0 0021

t	$\frac{x}{2} \times 10^3$	$\text{LOG} \frac{c}{c - \frac{x}{2}}$	Δ_1	Δ_2	$f(x)$ (EXPTL)	$f(x)$ (CALCD)	$\delta \times 10^4$	$\delta_t \times 10^3$
minutes								
0.067	0.107	0.0153	0.0024	0 0001	0.0176	0 0169	+7	+3
0.337	0 436	0 0662	0 0095	0 0005	0.0752	0.0766	−14	−6
0 670	0.817	0.1338	0 0175	0 0009	0.1504	0.1502	+2	+1
1.003	1 146	0.2016	0 0243	0 0012	0.2247	0.2239	+8	+4
1.335	1.419	0.2681	0 0298	0.0015	0.2964	0.2973	−9	−4
1 668	1 668	0.3380	0 0348	0 0018	0.3710	0 3709	+1	0
1.998	1 866	0 4047	0.0387	0 0020	0 4414	0.4439	(−25)	(−11)

The results of two series of experiments are given in tables 6 and 7. Table 8 gives a survey of six series in glycolate buffers and fourteen series in acetate buffers. The sixth column in tables 6 and 7 contains $f(x)$ found from the experiments. The seventh column gives $f(x)_{\text{calcd}} = k^*t + S$, calculated for all the values of t and the values of k^* and S found in the series. The experiments agree well with formula 38. This is seen from the next to the last column, where $\delta = f(x) - f(x)_{\text{calcd.}}$ is given. δ is usually small. Only when much more than half of the acetoacetic acid is brominated may we get a considerable deviation. A disappearance of titratable bromine also takes place here, although at a much later stage than in hydrochloric acid. This is seen from table 7. Here the experiments still agree with the formula when 73 per cent of the reaction has

taken place ($t = 0.353$). While the titratable bromine at the time $t = 2$ corresponds to 99 per cent of the acetoacetic acid, it has at the time $t = 5$ fallen to 80 per cent.

The velocity is often so great that it is difficult to follow the reaction. Thus the time of half-completion varies from 6 to 22 seconds in the experiments at 18°C. Probably a considerable part of the unsystematic error is due to errors in the determination of the time when the reaction is started and stopped. When we introduce into formula 38 the values of k^* and S found in a series of experiments, we may calculate t for each of the experimental values of $f(x)$. The difference δ_t between the experimental and calculated values of t may also be found from the expression

TABLE 7

Bromination of acetoacetic acid in a mixture of acetic acid and sodium acetate at 17.94°C.

$g = 0.2018$	$b = 0.1042$	$c = 0.003083$	$(KBr) = 0.050$
$(C_2H_5OH) = 0\ 0031$	$s = 0.154$	$L = 14.62$	$(H^+) = 0.0000$
$\gamma_\infty = 0\ 06759$	$\gamma_0 = 0\ 06353$	$\gamma_m = 0.06556$	$f_0 = 0.0043$
$f_{R^-} = 0.322$	$E = 0\ 0943$	$F = 0\ 0780$	$M = 0\ 835$
$N = 0\ 0495$	$k^* = 1\ 602$	$k_{B^-}{}^* = 232$	$S = 0.0059$

t	$\frac{x}{2} \times 10^1$	$\text{LOG}\frac{c}{c-\frac{x}{2}}$	Δ_1	Δ_2	$f(x)$ (EXPTL)	$f(x)$ (CALCD)	$\delta \times 10^1$	$\delta_t \times 10^3$
minutes								
0 053	0 571	0.0889	0.0022	0.0002	0.0909	0 0908	+1	0
0.097	0.943	0.1587	0.0036	0.0003	0.1620	0 1613	+7	0
0.120	1.118	0.1955	0.0043	0.0003	0.1995	0.1981	+14	+1
0.162	1.384	0.2587	0.0053	0 0004	0.2636	0.2654	−18	−1
0.203	1.629	0.3257	0.0063	0.0005	0.3315	0.3311	+4	0
0 353	2 238	0.5625	0.0085	0.0006	0.5704	0.5714	−10	−1
1.003	3 030	1 790	0.0114	0.0009	1.800	1 613		
2.000	3 054	2.074	0.0115	0.0009	2 085	3.210		
5.000	2.47							

$\delta_t = \delta/k^*$. δ_t is given in the last column of tables 6 and 7. The average deviation for all the experiments has been calculated from the formula $\delta_{tm} = \sqrt{\frac{\Sigma\delta_t^2}{n-1}}$, where n is the number of experiments. In the calculation we have omitted experiments where more than 60 per cent of the reaction has taken place, because in the last part of the reaction great deviations of another origin are found. In this way we find from ninety experiments $\delta_{tm} = 0.0026$ minute or 0.15 second. From table 8 we see that $k_{B^-}{}^*$ is, to a good approximation, constant at constant temperature for each of the catalysts.

In each series we have determined the constant S (expression 46). Owing to the great velocity the value is very rough. If we calculate ϵ_i,

the degree of enolization of the acetoacetate ion, from S found in the experiments at 0°C. and $\epsilon = 0.0073$, we get the values given in the last column of table 8. The mean value of thirteen determinations is $\epsilon_i = 0.0045$ with an average error of 0.0005. In spite of the rather small unsystematic error, we take reservation for the reliability of this value.

TABLE 8

Bromination of acetoacetic acid in glycolate and acetate buffer solutions

All solutions contain KBr, 0.050 M

BUFFER	TEMPERATURE	$c \times 10^1$	s	$(HB)_{t=\infty}$	$(B^-)_{t=\infty}$	γ_0	γ_∞	k^*	$k_{B^-}{}^*$	$\epsilon_i \times 10^4$
	degrees C.									
Glycolate	0.03	3.08	0.128	0.02094	0.0719	0.1110	0.1353	0.2211	19.4	45
		2.87	0.129	0.02344	0.0729	0.1250	0.1472	0.2429	19.4	42
		2.87	0.204	0.0446	0.1484	0.1292	0.1403	0.4279	19.0	48
		2.87	0.204	0.0832	0.1484	0.2218	0.2334	0.722	19.3	38
		2.87	0.204	0.1220	0.1484	0.2969	0.3085	0.956	19.3	52
	17.94	2.87	0.129	0.02344	0.0729	0.1326	0.1564	1.084	81.4	
Acetate	0.03	3.34	0.154	0.0517	0.0973	0.02981	0.03293	0.1844	55.1	50
		3.33	0.104	0.0520	0.0475	0.05802	0.06626	0.1881	54.8	44
		3.33	0.154	0.1013	0.0973	0.05856	0.06257	0.3478	54.7	54
		6.66	0.158	0.1041	0.0945	0.05760	0.06584	0.3631	55.9	42
		3.33	0.254	0.2003	0.1976	0.05776	0.05972	0.6552	54.3	39
		3.34	0.154	0.2006	0.0973	0.1109	0.1167	0.6478	54.6	42
		3.33	0.104	0.2016	0.0473	0.1995	0.2161	0.6151	55.1	40
		6.65	0.108	0.2044	0.0445	0.1945	0.2287	0.6270	56.3†	
		3.33	0.254‡	0.2016	0.0474	0.2022	0.2106	0.6011	55.3	48
	17.94	3.08	0.104	0.0514	0.0475	0.06086	0.06891	0.814	228	
		3.08	0.104	0.0528	0.0477	0.06232	0.07044	0.878	240	
		3.09	0.154	0.1005	0.0980	0.06160	0.06556	1.538	229	
		3.08	0.154	0.1038	0.0980	0.06353	0.06759	1.602	232	
		3.08	0.254	0.1978	0.1978	0.06206	0.06401	3.01	233	

Mean values of $k_{B^-}{}^*$: Glycolate catalysis, 19.3 at 0.03°C, 81.4 at 17.94°C. Acetate catalysis, 55.0 at 0.03°C., 232 at 17.94°C.

† Omitted, when taking the mean value, because the series is considered less accurate.

‡ Containing NaCl, 0.150 M.

VI. GENERAL BASIC CATALYSIS OF THE ENOLIZATION OF ACETOACETIC ACID

All the experimental evidence on the bromination of acetoacetic acid to α-monobromoacetoacetic acid confirms the assumption that the velocity of this reaction is determined by the enolization of the undissociated part of the acetoacetic acid, which reaction is catalyzed by bases in general. No acid catalysis was found. The theory of general basic catalysis and

prototropic isomerization was discussed in another paper (4), where references to the literature may be found. According to the theory the velocity of enolization is determined by the velocity with which the proton in the alpha position to the carboxyl group is transferred to the basic catalyst. We found by experiment that the enolization of the ions of acetoacetic and monobromoacetoacetic acids is very slow in comparison with that of the undissociated acids. This is in agreement with the theory because the proton, owing to the free negative charge, is bound much more firmly in the ions than in the neutral acids. When the basic catalyst has a negative charge the electrostatic repulsion will further counteract the reaction of the ion.

TABLE 9

Basic catalysis of the enolization of acetoacetic acid at 0 and 18°C.

$\beta = 0.50$

TEMPERATURE	CATALYST	p	q	$K_{\hat{H}B}$	$\log\left(\frac{p}{q}K_B^0\right)$	$k_{B^-}{}^*$	$\log\left(\frac{1}{q}k_{B^-}{}^*\right)$	G^*	Q (0 to 18°C)
degrees C									
0.03	$CH_3CO_2^-$	1	2	1.70×10^{-5}	4.469	55.0	1.439	0.160	12.7
	$CH_2OHCO_2^-$	1	2	1.36×10^{-4}	3.566	19.3	0.985	0.159	12.7
	$CH_3COCH_2CO_2^-$	1	2	2.57×10^{-4}	3.289	16.9	0.927	0.192	13 1
	H_2O	1	1	55.5	−1.74	0.00425	0.628-3	0.0315	12.7
17.94	$CH_3CO_2^-$	1	2	1.79×10^{-5}	4.447	232	2.065	0.694	
	$CH_2OHCO_2^-$	1	2	1.48×10^{-4}	3.528	81.4	1.610	0.702	
	$CH_3COCH_2CO_2^-$	1	2	2.62×10^{-4}	3 281	74.7	1.572	0.855	
	H_2O	1	1	55.5	−1.74	0.0180	0.255-2	0.133	

The "uncatalyzed" reaction may be explained as the result of the basic catalysis of water. If we neglect the effect of the association of the water molecules, $k_{H_2O} = k_0/55.5$, and the basic strength of water $K_{H_2O} = 55.5^{-1}$. In the experiments we have thus determined the catalytic constants of the four bases acetate, glycolate, and acetoacetate ions, and water.

In other reactions catalyzed by bases in general it has been found that the following formula holds approximately (see reference 4).

$$\frac{1}{q} k_B = G\left(\frac{p}{q} K_B{}^0\right)^\beta \tag{47}$$

Here K_B^0 is the basic strength of the catalyst at infinite dilution, p and q are statistical factors for the base, and β and G are constants characteristic of the reaction. In order to test the formula for the reaction here ex-

amined we plot log $\left(\frac{1}{q}k_B^*\right)$ against log $\left(\frac{p}{q}K_B^0\right)$ (see table 9 and figure 3). If we determine β from the catalysis of acetate and glycolate ions we get $\beta = 0.503$ at 0°C. and $\beta = 0.495$ at 18°C. Thus β is practically independent of the temperature. For the calculation of G from formula 47 we have used $\beta = 0.50$ (table 9). In figure 3 we have at both temperatures drawn straight lines with the slope 0.50 through the points for the acetate catalysis. The points for the acetoacetate catalysis fall a little above the lines, while those for the water catalysis fall a good deal below them. As seen from table 9 the catalysis of the acetoacetate ion is 20 per cent stronger than we find from formula 47 when we base the calculation on the acetate

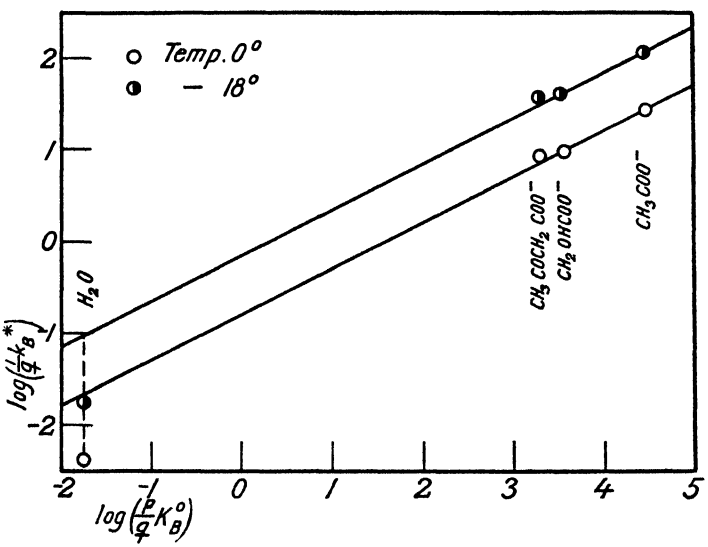

FIG. 3. BASIC CATALYSIS OF THE ENOLIZATION OF ACETOACETIC ACID

and glycolate ion catalysis. The water catalysis is only one-fifth of the calculated value. The deviation is in both cases practically independent of the temperature. Table 9 also gives the heat of activation Q in kilogram-calories calculated in the usual way. Q is practically the same for all the catalysts.

VII. SUMMARY

The bromination of acetoacetic acid was studied in hydrochloric acid and in different buffer solutions. The experiments could always be explained from the assumption that the rate of bromination is determined by the enolization of the undissociated acetoacetic acid and α-mono-

bromoacetoacetic acid, which reactions are catalyzed by bases in general, but not by acids.

The bromination was studied at 0°C. in hydrochloric acid of different concentration. The reaction follows scheme 1a-1d. From the experiments were calculated the unimolecular velocity constants for the enolization of acetoacetic and monobromoacetoacetic acids (the "uncatalyzed" or water reaction), and the dissociation constant of the latter acid.

The bromination of mixtures of acetoacetic acid and sodium acetoacetate was studied at 0 and 18°C. The gross reaction is expressed by scheme 7. The velocity is determined by the enolization of the undissociated acetoacetic acid. The velocity constant for the "uncatalyzed" reaction and the catalytic constant for the acetoacetate ion catalysis of the enolization were computed.

The bromination of acetoacetic acid in glycolate and acetate buffer solutions was studied at 0 and 18°C. The gross reaction is expressed by scheme 17. From the experiments were calculated the catalytic constants for the glycolate and acetate ion catalysis of the enolization of acetoacetic acid.

The dependence of catalytic constant upon basic strength was examined.

My thanks are due to Professor Niels Bjerrum for his kind interest in my work.

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THE INFLUENCE OF SALTS UPON INTERMITTENT PHOTOGRAPHIC EXPOSURES

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If, after an initial exposure sufficient to produce considerable developable density, a photographic emulsion is subjected to a second exposure to light of usually longer wave length, the existing density may be decreased. This is the Herschel effect.

Narbutt (10) has made a comprehensive study of the influence of various ions upon the Herschel effect. He concludes that the Herschel effect (with Satrox Universal Paper) is very strongly increased by the presence of Cu^{++}, Fe^{+++}, and VO^{++}. The remaining cations (of those investigated) have no marked effect. In the case of anions, F^- has little effect, Cl^- increased the Herschel effect considerably, and Br^- increased it very markedly. The anions CH_3COO^-, NO_3^-, and SO_4^{--} have no appreciable influence.

In general, both Narbutt and Trivelli (12) have found that the greater the decrease in sensitivity produced by a given ion, the correspondingly greater was the Herschel effect, and vice versa.

Perhaps during a photographic exposure two reactions exist, one a forward reaction making the silver halide grain developable, and the other a reverse reaction converting developable grains to their original state. The Herschel effect has been explained as the result of the preponderance of the reverse reaction. These and somewhat similar suggestions have already been reported (2, 3, 5, 6, 7, 8, 11). If we assume that a decrease in sensitivity is accompanied by an increase in the speed of the reverse *relative* to that of the forward reaction, the observations of Narbutt and Trivelli are explained.

Blair and Hylan (1) have suggested that the reactions (forward and reverse) which take place during exposure continue for a short time after the exposure has ceased. On this basis they were able to explain the findings of Davis (4) and others that intermittent exposures produce developable densities differing from those produced by equal continuous exposures. The reverse reaction, in the majority of cases, predominates over the forward during the periods of darkness between the intermittent exposures, and the resulting density is accordingly in these cases smaller than that produced by an equal continuous exposure.

TABLE 1

Developable densities produced by equal continuous and intermittent exposures upon treated paper

TREATMENT OF PAPER	EFFECTIVE TIME OF EXPOSURE	INTERMITTENT SECTOR OPENING	DENSITY BY CONTINUOUS EXPOSURE	DENSITY BY INTERMITTENT EXPOSURE	DENSITY RATIO
Unwashed	30	120°	1.53	1.445	1.06
	15	60°	1.29	0.80	1.61
	7.5	30°	0.54	0.21	2.52
Washed 1 hour	30	120°	1.52	1.50	1.02
	15	60°	1.52	1.47	1.04
	7.5	30°	1.36	1.06	1.29
	3.75	15°	0.64	0.375	1.71
Na_2SO_4 (1.5 per cent)	30	120°	1.50	1.46	1.02
	15	60°	1.37	1.09	1.26
	7.5	30°	0.745	0.39	1.91
K_2SO_4 (1.5 per cent)	30	120°	1.54	1.54	1.00
	15	60°	1.49	1.46	1.02
	7.5	30°	1.31	1.03	1.27
	3.75	15°	0.59	0.29	2.00
$NiSO_4$ (1.5 per cent)	30	120°	1.53	1.53	1.00
	15	60°	1.50	1.43	1.05
	7.5	30°	1.16	0.80	1.45
	3.75	15°	0.57	0.315	1.81
KF (1.5 per cent)	30	120°	1.56	1.55	1.02
	15	60°	1.52	1.47	1.03
	7.5	30°	1.345	1.03	1.31
	3.75	15°	0.61	0.415	1.47
KCl (1.5 per cent)	90	120°	1.50	1.37	1.10
	45	60°	1.29	0.74	1.74
	22.5	30°	0.50	0.19	2.59
KBr (1.5 per cent)	360	120°	1.49	1.46	1.02
	180	60°	1.46	1.32	1.11
	90	30°	1.37	1.01	1.36
	45	15°	1.15	0.54	2.11
	22.5	7.5°	0.80	0.23	3.52
$CuSO_4$ (1.3 per cent)	240	120°	1.52	1.53	1.00
	120	60°	1.50	1.40	1.07
	60	30°	1.26	0.71	1.77
	30	15°	0.56	0.15	3.71

TABLE 1—*Concluded*

TREATMENT OF PAPER	EFFECTIVE TIME OF EXPOSURE	INTERMITTENT SECTOR OPENING	DENSITY BY CONTINUOUS EXPOSURE	DENSITY BY INTERMITTENT EXPOSURE	DENSITY RATIO
Ferric ammonium sulfate (0.6 per cent)	840	120°	1.47	1.295	1.13
	420	60°	1.40	1.13	1.24
	315	30°	1.32	0.84	1.58
Silver nitrate plus citric acid (1 per cent each)	10	120°	1.51	1.47	1.03
	5	60°	1.41	1.38	1.02
	20	120°	1.49	1.49	1.00
	10	60°	1.44	1.41	1.03
	10	120°	1.27	1.35	0 94
	5	30°	1.225	1.21	1.01
	5	60°	1.15	1.07	1.07
	2.5	30°	0.95	0.98	0.97
	2.5	60°	0.523	0.495	1.06
$(NH_4)_2SO_4$ (0.8 per cent)	30	120°	1.50	1.45	1.04
	15	60°	1.45	1.36	1.07
	7.5	30°	1.23	0.99	1.24
Lead acetate (1.2 per cent)	30	120°	1.56	1.56	1.00
	15	60°	1.51	1.45	1.04
	7.5	30°	1.10	0.79	1.39
	30	30°	1.55	1.52	1.02
	15	15°	1.48	1.375	1.08
	7.5	7.5°	1.24	0.95	1.31
Sodium acetate (1.5 per cent)	15	60°	1.50	1.41	1.07
	7.5	30°	1.24	0.90	1.37
	3.75	15°	0.62	0.33	1.87
Ammonium chloride (1.5 per cent)	60	120°	1.37	1.365	1.01
	30	60°	1.21	0.80	1.52
	15	30°	0.47	0.24	1 95

The present paper deals with the influence upon the intermittency effect of many of the salts used by Narbutt, and in addition, certain other salts whose action upon the Herschel effect is known.

EXPERIMENTAL

A sensitized paper, Eastman Azo F No. 5, very strongly subject to intermittency effects, was used in this investigation. This paper was washed in gently running water for one hour to remove soluble salts. The paper was dried and immersed for ten minutes in various salt solutions and again dried. Each sheet was cut into two parts, one of which was

given a series of intermittent exposures, and the other half a corresponding series of continuous exposures of the same total energy. Duplicate runs were made throughout.

The exposing light was diffused white radiation from an incandescent lamp. The intensity at the paper was 420 ergs per cm.^{2} per second. The intermittent exposures were obtained by means of a sector wheel placed directly in front of the emulsion. The apertures of this wheel were 120°, 60°, 30°, 15°, and 7.5°. The wheel was driven by a synchronous motor at the rate of 0.312 revolutions per second.

The exposed paper was developed for 90 seconds in elon–hydroquinone developer (D73), diluted one to three. The densities recorded are normal reflection densities.

Table 1 gives the results obtained with various salts at the dilutions specified. Each density value given is the mean of the duplicate runs except in the case of the silver nitrate–citric acid mixture. Owing to experimental difficulties in this case the individual variation was much greater than in the other determinations, and individual results of three runs are recorded.

DISCUSSION

In order to show more clearly the effect of salts upon intermittency, the data given in table 1 are plotted in figures 1 to 4. The densities produced by the continuous exposures are plotted as abscissae and the ratios of the densities produced by continuous and intermittent exposures as ordinates.

Figure 1 shows the result of washing upon the intermittency effect. The speed of the emulsion is increased (table 1) and the intermittency effect decreased. These differences are due primarily to the removal of soluble salts by washing, but they are probably partly due to the effect of water upon the emulsion itself.

Figure 2 indicates the method employed to isolate the effect of the individual ions (following the procedure of Narbutt in his study of the Herschel effect). Nickel sulfate, sodium sulfate, and potassium sulfate all produce practically no effect. Hence, it must be assumed that either the anions and cations have no effect separately, or that their effects are equal and opposite. The anions are the same in each case, while the cations differ considerably in properties. The assumption that these individual ions are without effect is accordingly the more plausible. This is further substantiated by the fact that sodium acetate is likewise without effect.

Figure 3 shows the effect of the halogen ions. The effect of I^- was to decrease the sensitivity to such an extent that data could not be obtained for paper treated with potassium iodide. The sequence here is the same as that found by Narbutt for their influence upon the Herschel effect.

A comparison of figures 3 and 4 will show that Cu^{++} increases intermit-

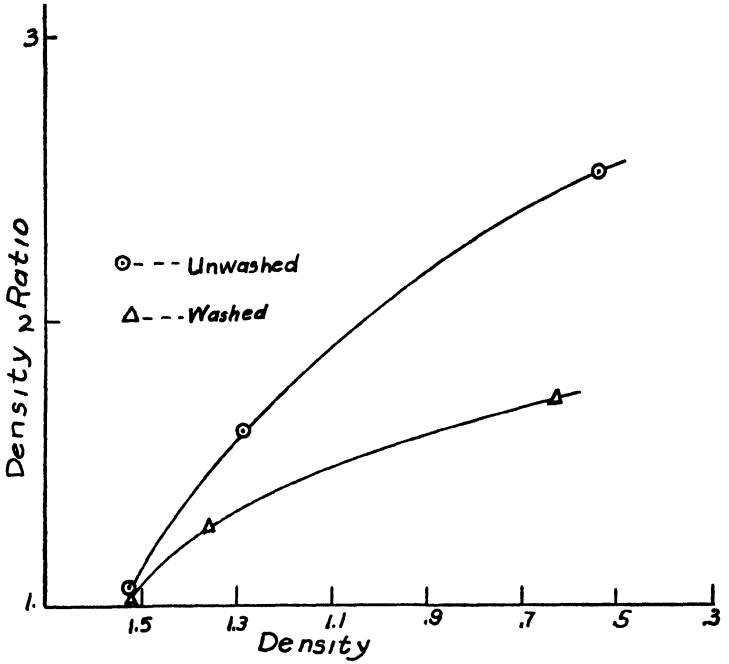

FIG. 1. THE INFLUENCE UPON THE INTERMITTENCY EFFECT OF WASHING THE EMULSION FREE OF SOLUBLE SALTS

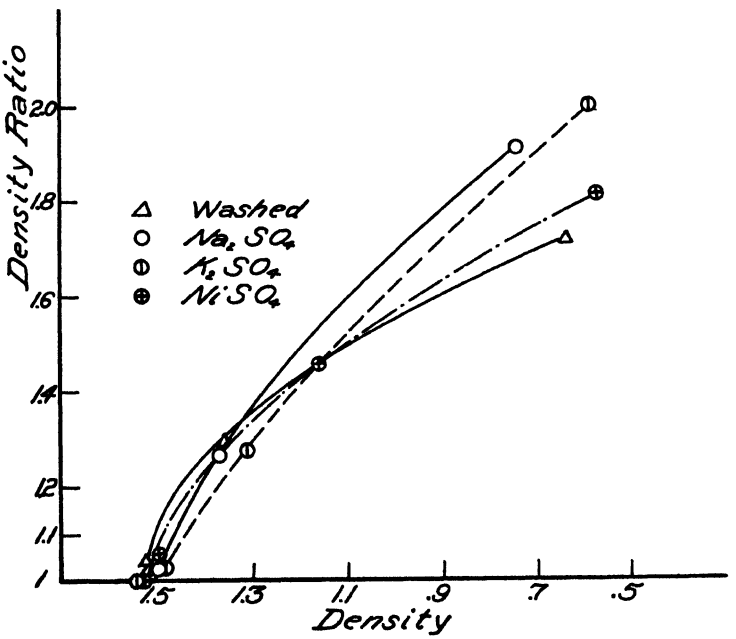

FIG. 2. THE ISOLATION OF THE IONIC EFFECTS INDICATING THAT Na^+, K^+, Ni^{++}, AND SO_4^{--} ARE NEUTRAL

tency effect almost as much as does Br^- for the concentrations used, whereas paper treated with a solution of 1 per cent silver nitrate and 1 per cent citric acid shows no intermittency effect. Lüppo-Cramer (9) has found that this solution prevents the Herschel effect, which again is in very good agreement with our initial thesis.

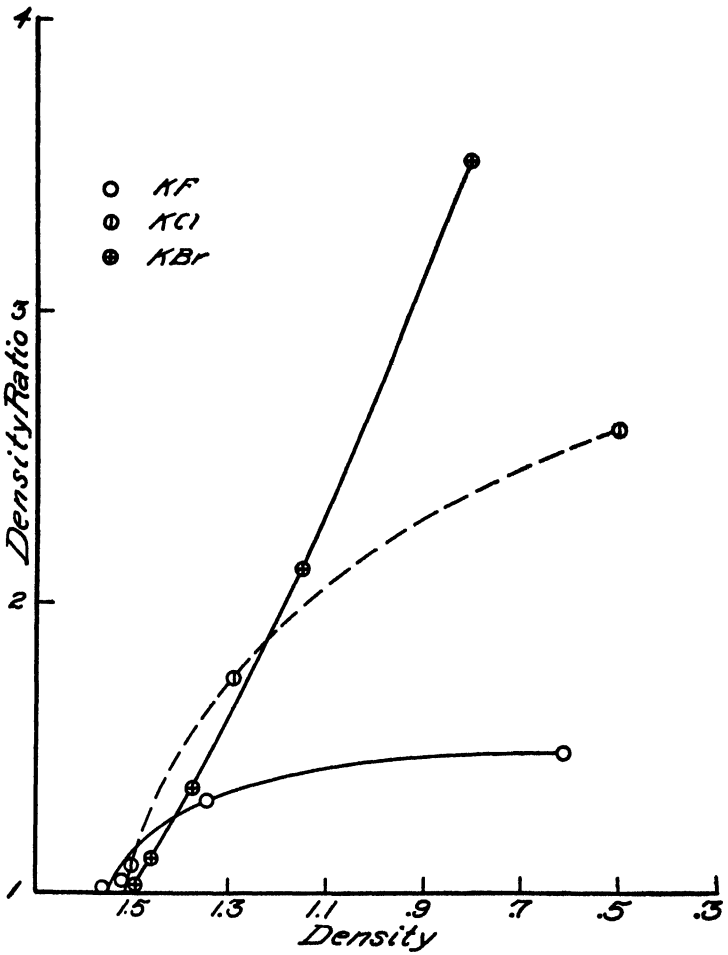

FIG. 3. THE ACTION OF THE HALIDE IONS UPON THE INTERMITTENCY EFFECT

The effects of the remaining ions were small. The ammonium ion apparently decreases the intermittency effect slightly, but a discoloration of the gelatin which invariably accompanied treatment with ammonium salts may, perhaps, make the results less reliable in this case. It is noteworthy, however, that these results are in agreement with those of Narbutt.

Pb^{++} likewise produced a small decrease in the intermittency effect, again in agreement with Narbutt. The remainder of the ions studied had practically zero effect.

In conclusion, it should be emphasized that not a single case was found in which the action of salts upon the Herschel effect, as reported by Nar-

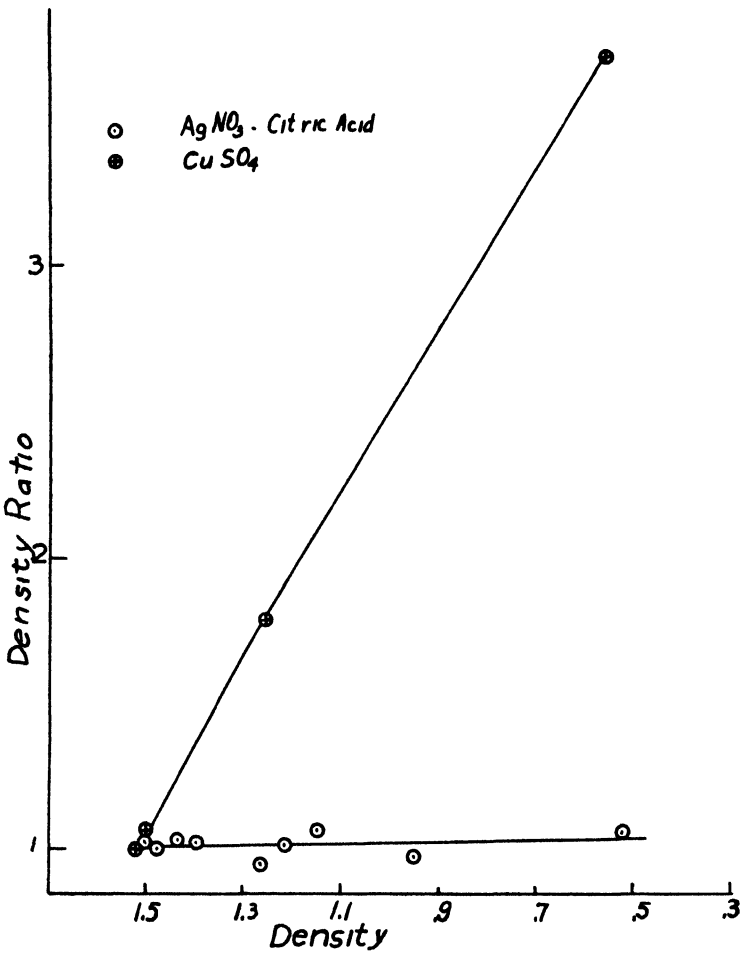

FIG. 4. THE ACTION OF Ag^{+} AND Cu^{++} UPON THE INTERMITTENCY EFFECT

butt, did not correspond to the action of the same salt upon the intermittency effect. Even the action of Ag^{+}, as found by Lüppo-Cramer upon a very different emulsion than the one we used (one very subject to Herschel effect, however), was the same. The general observations of Narbutt as to the relation which exists between the influence of an ion upon the

Herschel effect and its influence upon sensitivity of the emulsion evidently carries over to the intermittency effect. Accordingly, we feel safe in predicting that, in general, any salt which acts as a sensitizer or desensitizer for the Herschel effect will act in the same capacity for the intermittency effect.

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THE KINETICS OF THE REACTION BETWEEN GASEOUS METHYL ALCOHOL AND NITROUS OXIDE

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INTRODUCTION

In view of the progress that is being made in the study of the kinetics of gaseous oxidations by molecular oxygen, it is of interest to extend the field of investigation to include similar reactions in which oxygen is replaced by other gases.

Dixon and Higgins (1) measured the temperatures of spontaneous ignition of jets of different combustible gases in an atmosphere of nitrous oxide, and found that these temperatures were usually slightly lower—in the case of hydrogen considerably lower—than those obtained with oxygen. Since such experiments involve great uncertainty as to gas composition, they cannot yield definite kinetic conclusions, but they seem to indicate that the mechanisms of the two oxidation processes are similar.

In the case of the hydrogen–nitrous oxide reaction, Hinshelwood (4) concluded that the rate of the reaction was no greater than could be accounted for by the decomposition of nitrous oxide followed by rapid reaction of the oxygen and hydrogen. Melville (7) has recently carried out an extensive investigation of this reaction. His measurements showed that the reaction was from ninety to five hundred times as fast as the nitrous oxide decomposition, depending on the experimental conditions. The rate was directly proportional to the pressure of nitrous oxide and nearly independent of that of hydrogen, except when the nitrous oxide pressure was high. It was unaffected by nitrogen and argon. Increasing the diameter of the reaction vessel increased the velocity of the reaction. These facts are satisfactorily explained by a chain mechanism, and in this regard there is therefore a resemblance to the hydrogen–oxygen reaction.

It seems desirable to extend such investigations to other systems, and the present paper deals with the oxidation of methyl alcohol by nitrous oxide. The corresponding reaction with oxygen is of the chain type, and has been investigated fairly thoroughly by Fort and Hinshelwood (2).

APPARATUS

The reaction was followed in the usual way by observing the rate of change of pressure in a system of constant volume. The apparatus was similar to that used in previous investigations (3, 8). The gases were introduced in the desired proportions into a mixing bulb, and were then allowed to expand into the evacuated reaction vessel. Pressures were read on a capillary manometer, the dead space being about 2 per cent of the volume of the reaction bulb. The reaction vessel was a more or less spherical Pyrex bulb having a volume of about 200 cc. To prevent condensation of water vapor the capillary manometer and connecting tubing were kept at 65°C. by means of electrical heating. The reaction bulb was contained in an electric furnace, the temperature of which was kept constant to within 1°C. by the hand regulation of rheostats. Temperatures were measured by means of a chromel–alumel thermocouple.

The methyl alcohol used was obtained by the fractionation of commercial methanol, and distilled between 64.8°C. and 65.0°C. (uncorr.). Nitrous oxide was obtained in cylinders from the Ohio Chemical and Manufacturing Co., and was used without purification.

EXPERIMENTAL

Between runs the reaction vessel was evacuated for about one hour, the pressure being reduced to about 10^{-4} mm. As will appear later, all experiments were not strictly reproducible, but it was found that the time of pumping and degree of vacuum obtained had no effect on the rate of the following run.

DECOMPOSITION OF ALCOHOL

It is first of all necessary to show that the reaction under investigation is not the mere decomposition of methyl alcohol and of nitrous oxide. Blank experiments showed that even at the highest temperatures used the decomposition of nitrous oxide was barely detectable after thirty minutes. The rate of alcohol decomposition, however, was appreciable, occurring under various conditions of temperature and pressure at rates from one-fourth to one-twentieth of that of the main reaction. The rate of the alcohol decomposition was very sensitive to changes in the condition of the wall of the vessel. In general very low rates were obtained after the bulb had been used for several runs with nitrous oxide–methyl alcohol mixtures, and the rate increased progressively when a series of runs was made with alcohol alone. It would therefore be extremely difficult to make any accurate correction for the alcohol decomposition during the main reaction because of the variability of the rate of its decomposition, and also because its decomposition products might be oxidized. No correction has been made

therefore, but the error thus introduced is probably not large. Some typical pressure–time curves for nitrous oxide–alcohol mixtures, and for alcohol alone are given in figure 1.

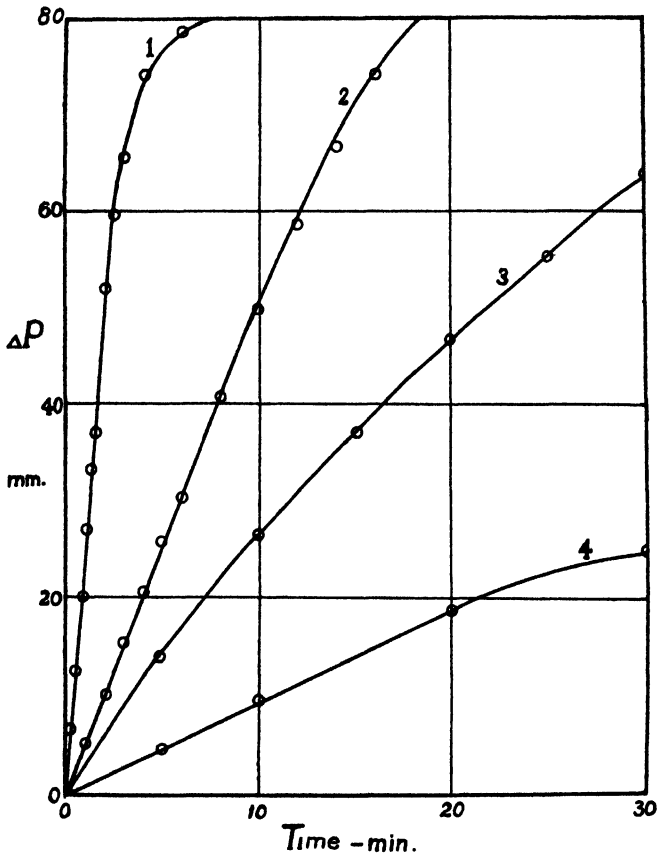

FIG. 1. TYPICAL TIME–PRESSURE CURVES AT 570°C.

Curve 1, 200 mm. nitrous oxide and 50 mm. methyl alcohol, packed bulb; curve 2, 200 mm. nitrous oxide and 50 mm. methyl alcohol, unpacked bulb; curve 3, 75 mm. methyl alcohol, packed bulb; curve 4, 75 mm. methyl alcohol, unpacked bulb.

THE PRESSURE CHANGE ACCOMPANYING THE REACTION

For the alcohol decomposition the average pressure increase when the reaction had reached completion was 126 per cent. In the case of nitrous oxide–alcohol mixtures the increase under all conditions was from 170 to 180 per cent of the initial partial pressure of alcohol. Had it not been for the accompanying decomposition of the alcohol the change would therefore have been about 200 per cent, provided that the decomposition products of the alcohol were not oxidized.

THE NITROUS OXIDE–METHYL ALCOHOL REACTION

Typical pressure–time curves are given in figure 1, and the data for a few typical runs in table 1.

The rates of reaction under various conditions have been compared by comparing the time required for a pressure increase equal to the initial alcohol content (t_{100}). The values of t_{100} for various mixtures at 570°C.

TABLE 1

Data for typical runs at 570°C.

Ratio N_2O/CH_3OH	5 1	4 1	3:1	2 1	1 5 1
P_{CH_3OH} in mm.	48	51	56	48	52
Per cent pressure increase at completion relative to CH_3OH	174	174	—	176	177
TIME	ΔP				
minutes	*mm*	*mm.*	*mm*	*mm.*	*mm.*
0	0	0	0	0	0
1	4.8	5.6	4.8	2.9	3.0
2	11.8	11 8	9.4	6 5	5.6
3	18 0	17.6	14.2	8.7	9.0
4	23.6	23.6	19.2	12.5	12.8
5	30.0	28 8	22.4	16 3	16.0
6	35.8	33.6	28.2	19 7	19.2
7	41.2	38.6	—	—	—
8	46.6	43.2	37 2	26.1	26.0
9	51.4	47.6	—	—	—
10	56.6	51.6	45.4	32 7	32 0
12	64.6	59.6	54.4	38.7	38.2
14	74.2	65.8	62.2	44.9	44 0
16	80.6	71.8	69.6	49.9	49.4
18	82.8	77.2	75.8	54.7	54.4
20	83.4	81.6	81.4	59.1	59.0
25	83.6	88.6	—	69 7	67.8
30	83.6	88.6	—	75 1	75.2
35	83 6	88 6	—	82 7	85.0
40	—	—	—	84.3	89.2
50	—	—	—	84.3	92 0

are given in table 2. If these times are to be strictly comparable it is essential that the pressure–time curves should be of the same general form under all conditions, i.e., that the curves are affine. To test this, pressure–time curves for a number of runs chosen at random are plotted in figure 2. The time scales are varied so that some one point, other than the origin, is common to all of them. It will be seen that they coincide throughout their entire length.

REPRODUCIBILITY

The rates of reaction were not always strictly reproducible. This is undoubtedly due to the condition of the surface of the bulb. A very small amount of carbon was deposited during the reaction, and while the amount was unimportant in itself, it probably accounts for the variability of the surface. After a reaction bulb had been in use for some time there was no marked drift in the rate of reaction. Some of the earlier results with each reaction bulb have therefore been discarded.

TABLE 2

Values of t_{100} for various mixtures at 570°C.

N_2O/CH_3OH	P_{CH_3OH}	t_{100}	N_2O/CH_3OH	P_{CH_3OH}	t_{100}
	mm.	*minutes*		*mm.*	*minutes*
5	58.3	7.8	3	17.8	10.9
5	48.0	8.3	3	10.9	10.0
5	41.4	8.9	3	9.8	9.7
5	38 4	8.6	2	80.0	14.8
5	35 4	8 5	2	67.2	15.5
5	29.7	8.3	2	56.7	15.6
5	24 5	8.2	2	48.0	15.3
5	21 0	8.3	2	28.3	13.4
5	14.7	7.6	2	20.2	12 9
5	7.4	6 9	2	18 0	13 0
4	50 8	9.9	2	14 0	12 3
4	32 5	9.8	2	10 4	12 3
4	23 4	9 8	1.5	74 3	16 8
4	20 0	9 5	1.5	62.5	17.2
4	12.5	8.6	1.5	51.8	17 0
4	11 3	8.7	1.5	45 8	16.4
3	56.4	12 5	1.5	44 0	15 7
3	36.7	12.0	1.5	27.8	14 9
3	36.5	11.8	1.5	21.1	14 9
3	27.6	12.0	1.5	12.7	13.6
3	20.7	11.0	1.5	10 2	14.0

EFFECT OF COMPOSITION

In figure 3 the values of t_{100} are plotted against the initial partial pressures of alcohol for various nitrous oxide–methyl alcohol mixtures at 570°C. From these curves it is possible to construct a set of single reactant curves showing the effect of varying the pressure of one reactant while the other remains constant. This is done in figure 4. It will be seen that t_{100} is approximately inversely proportional to the concentration of nitrous oxide,

and approximately proportional to that of alcohol. In other words, the rate can be approximately expressed by

$$\frac{-d(CH_3OH)}{dt} = K(N_2O)$$

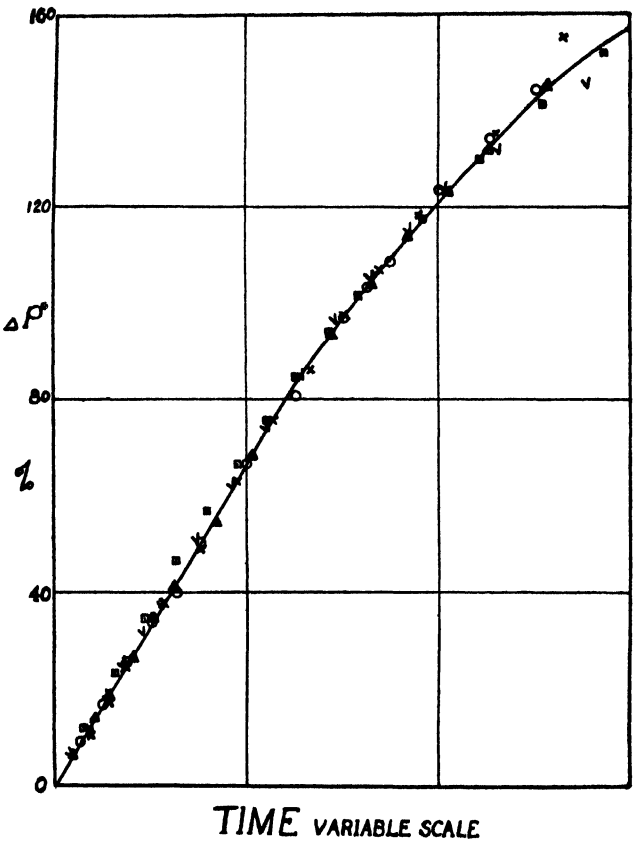

FIG. 2. AFFINE CURVES FOR VARIOUS NITROUS OXIDE–METHYL ALCOHOL MIXTURES AT 570°C.

TEMPERATURE COEFFICIENT AND EFFECT OF SURFACE

To determine the temperature coefficient of the reaction, a separate series of runs was made at different temperatures (in random order) with a mixture containing 50 mm. of alcohol and 200 mm. of nitrous oxide. Since the effect of packing the bulb on the rate of reaction is often the conclusive factor in determining the mechanism, a similar series was carried out with a reaction vessel packed with 1-inch lengths of Pyrex tubing. The surface

was thus increased about six times, although the two surfaces are not necessarily strictly comparable on account of the deposition of carbon during the reaction. The results are given in table 3. It will be seen that the rate of reaction is roughly proportional to the area of surface. A series of runs showed that packing increased the rate of alcohol decomposition to almost exactly the same extent as it increased that of the main reaction.

In figure 5, log t_{100} is plotted against $1/T$. The apparent heat of the activation calculated from the slope of these lines is 59,500 calories per gram-molecule for the empty bulb, and 52,000 for the packed bulb.

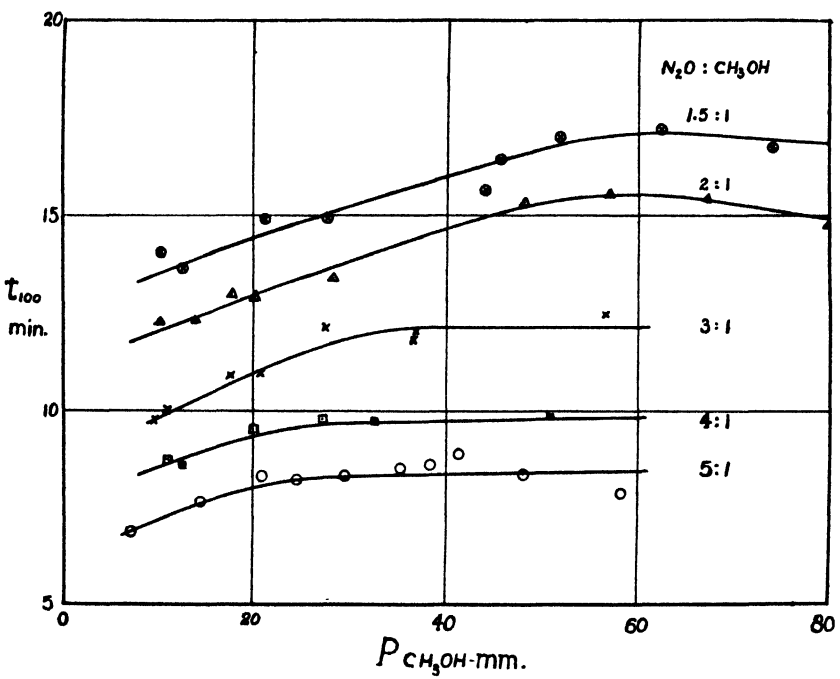

FIG. 3. THE EFFECT OF CONCENTRATION AT 570°C.

THE COURSE OF THE REACTION

The gaseous products analyzed were obtained mainly from runs made with the packed bulb at 570°C., and initial alcohol pressures of from 70 to 130 mm.

For the simple decomposition of methyl alcohol two analyses gave the following results: CO, 35.5, 33.8 per cent; CH_4, 2.0, 2.0 per cent; H_2, 61.5, 62.9 per cent. These results are in agreement with results given elsewhere (5) and indicate that the main reaction is

$$CH_3OH = CO + 2H_2$$

This, however, would require an expansion of 200 per cent, while that actually found was always about 126 per cent. It follows that a consid-

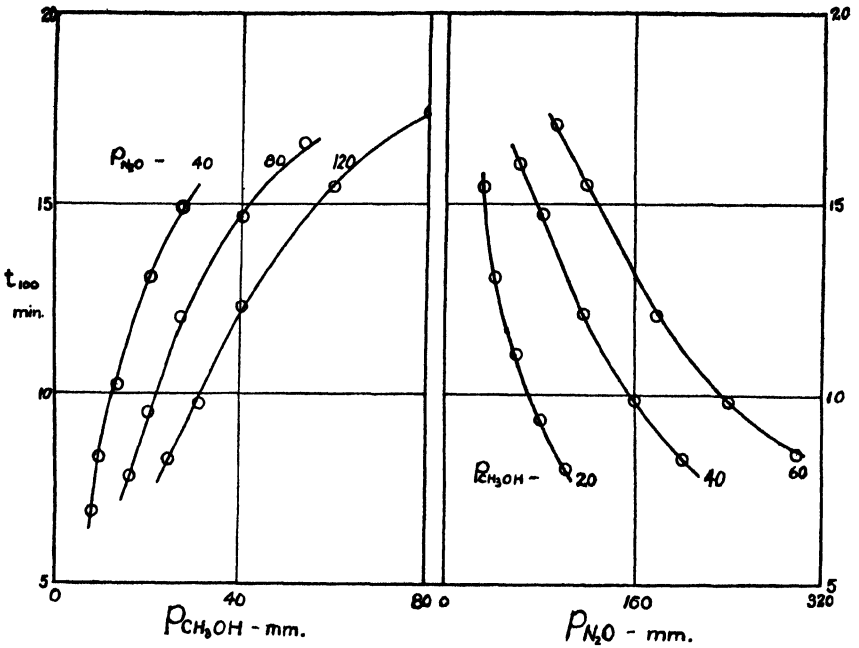

FIG. 4. THE EFFECT OF SINGLE REACTANTS AT 570°C.

TABLE 3

Temperature coefficient and effect of surface

TEMPERATURE	t_{100}		RATIO $\frac{\text{UNPACKED}}{\text{PACKED}}$
	Empty bulb	Packed bulb	
degrees C.	*minutes*	*minutes*	
500	162 195	26.1	6.8
520	90.8	9.1	10.1
535	48.5 49.0	6.8	7.2
550	22.4	4.3 4.7	5.0
570	9.3 10.2	1.83	5.4

erable amount of condensable products must be formed. Moreover, since the analysis shows a reasonably close balance between the constituents, the substances condensing out must have an empirical composition summing

up to approximately CH_4O. Since the alcohol decomposition is only a side reaction, it did not appear worth while investigating it further.

The analysis of the products of the nitrous oxide–alcohol reaction is complicated because of the solubility of nitrous oxide in all the customary absorbents (6). Inasmuch as the form of the reaction velocity curves is the same for all mixtures, the products of the reaction are almost certainly

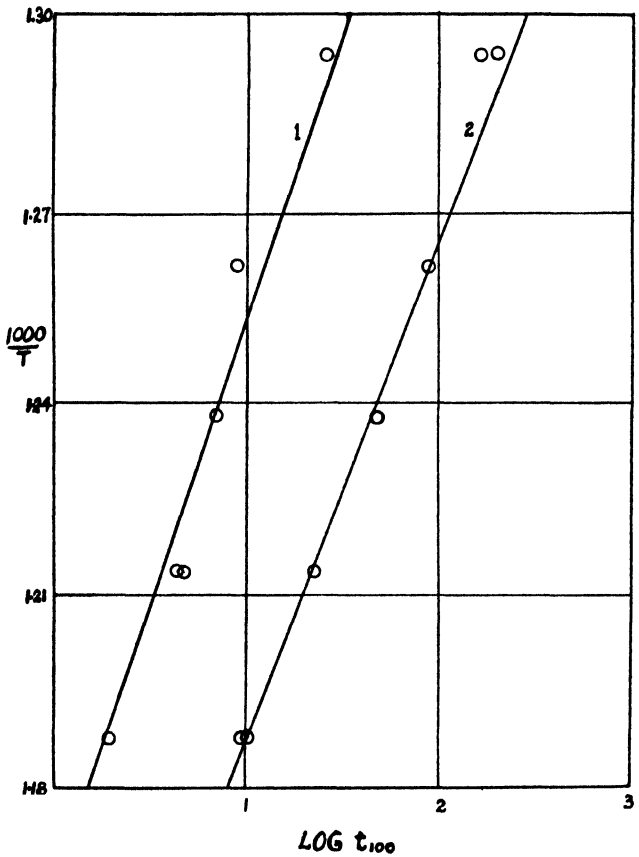

FIG. 5. TEMPERATURE COEFFICIENT

Curve 1, packed bulb; curve 2, unpacked bulb. $4N_2O + 1CH_3OH$. Total pressure, 250 mm.

independent of the $N_2O:CH_3OH$ ratio. Hence, in order to minimize the amount of nitrous oxide in the products, all analyses were made with a $1.5N_2O$ to $1CH_3OH$ mixture. The products thus obtained still contained some nitrous oxide. The solubility of this in potassium hydroxide and alkaline pyrogallol was not very serious, but fuming sulfuric acid and acid cuprous chloride dissolved so much nitrous oxide that they could not be

used. For this reason the gas left after absorption of carbon dioxide and oxygen was transferred directly to the combustion pipet and burned with oxygen. On the reasonable assumption that the gas at this stage contained only carbon monoxide, hydrogen, nitrous oxide, and nitrogen, it is possible to determine the amounts of the individual constituents. In order to obtain a check, and especially to determine whether any nitrous oxide were lost in the two absorbents used, some samples were burned without previous treatment, and the carbon dioxide and nitrogen in the product determined. Three such determinations from runs at 570°C. gave: $CO + CO_2$, 23.6, 26.5, and 24.3 per cent, average 24.8 per cent; $N_2 + N_2O$, 45.9, 44.9, and 45.2 per cent, average 45.3 per cent.

Two analyses by the more complete method gave:

CO_2	O_2	CO	H_2	N_2O	N_2	$CO_2 + CO$	$N_2 + N_2O$
3.7	1.5	19.3	28.1	8.9	38.5	23.0	47.4
4.0	1.3	19.3	26.7	11.3	37.3	23.3	48.6

It will be seen that the values for $CO + CO_2$ and $N_2 + N_2O$ are in satisfactory agreement with the values determined by direct combustion.

It is apparent that the ratio C:N is quite different from that which would be expected from the composition of the original mixture ($1.5N_2O + 1CH_3OH$). Thus if we use the values of nitrous oxide and nitrogen in the first analysis above to set up a material balance we have for the 94.8 parts of nitrogen,

	Carbon	*Hydrogen*	*Oxygen*
Calculated	31.6	126.4	79.0
Observed	23.0	56.2	38.6
Difference	8.6	70.2	40.4

The amount of carbon deposited in the reaction is far too little to account for the above. The missing hydrogen and oxygen are roughly in the proportions to form water. All three substances could be approximately accounted for by assuming $H_2O + HCHO$, but there was no evidence of an appreciable amount of formaldehyde, and in any case it is unlikely to be stable at such high temperatures.

If we use carbon as a basis for a balance, we have

	Nitrogen	*Hydrogen*	*Oxygen*
Calculated	69.0	92.0	57.5
Observed	94.8	56.2	38.6
Difference	25.8	35.8	18.9

Here the hydrogen and oxygen are almost exactly in the required proportions to form water. There is, however, a decided excess of nitrogen.

Suppose we assume that the primary reaction is

$$CH_3OH + N_2O = HCHO + H_2O + N_2$$

followed by

$$HCHO = H_2 + CO$$

and that we also have the side reactions

$$CH_3OH + N_2O = CO_2 + 2H_2 + N_2$$
$$2N_2O = 2N_2 + O_2$$

Then if we take CO = 19.3, CO_2 = 3.7, and O_2 = 1.5 as in the analysis, we have H_2 = 26.7, N_2 = 26.0, H_2O = 19.3, N_2O = 8.5. The actual analysis, averaging the H_2O on the basis of hydrogen and oxygen is CO = 19.3, CO_2 = 3.7, O_2 = 1.5, H_2 = 28.1, H_2O = 18.4, N_2O = 8.9, N_2 = 38.5. The agreement is very satisfactory, except for the excess N_2. It may therefore be concluded that the above scheme represents the general behavior, but that some condensation also occurs, the condensable material being oxidized in the process and hence liberating nitrogen.

There was no appreciable alteration in the products of reaction with changing temperature. Thus an analysis at 500°C. with a $1.5N_2O + 1CH_3OH$ mixture gave:

CO_2	O_2	CO	H_2	N_2O	N_2	$CO_2 + CO$	$N_2 + N_2O$
3.6	1.4	22.3	25.9	7.9	38.9	25.9	46.8

EXPLOSIONS

Attempts were made to obtain explosions in methyl alcohol–nitrous oxide mixtures at higher temperatures. In all cases there was merely a progressive increase in the reaction velocity with increasing temperature, without any sign of sharp limits.

DISCUSSION

The kinetic interpretation of the results is not without difficulty.

Since the rate of reaction is proportional to the surface area, it would appear at first sight that the reaction is of the ordinary heterogeneous type. If this is the case, then the approximate expression for the rate,

$$\frac{-d(CH_3OH)}{dt} = K(N_2O)$$

can be simply explained on the basis of fairly small adsorption of nitrous oxide. The heat of activation, however, is between 50,000 and 60,000 calories. This is somewhat larger than the value which would be expected for a homogeneous bimolecular reaction in the temperature region employed. It is consequently very high for a heterogeneous reaction. Moreover, if the reaction is a heterogeneous one, this is only the apparent heat of activation, and the true heat of activation must be higher than this. If the

reaction were strongly retarded by the products or by one of the reactants, the apparent heat of activation might be higher than the true one. The results, however, give no indication of such an effect. It is, however, possible that variations in the relative adsorptions of the reactants may account for the high apparent heat of activation. The heat of activation found is approximately equal to that of the dissociation of nitrous oxide. This can have no significance, however, since the reaction is not homogeneous.

In the hydrogen–nitrous oxide reaction Melville found that the rate was approximately given by

$$\frac{-d(H_2)}{dt} = K(N_2O)$$

In this reaction the chains are initiated by the decomposition of nitrous oxide. It is therefore tempting to assume that the nitrous oxide–methyl alcohol reaction is also a chain reaction, in view of the formal similarity of the expression for the rate and of the exothermic character of the reaction. If this were the case, however, it would be necessary to assume that, unlike the hydrogen–nitrous oxide reaction, the chains are initiated at the wall and broken in the gas. The high heat of activation could be explained on the basis of a variable chain length, which makes the temperature coefficient a composite one. There is, however, no real evidence for a chain mechanism, and the fact that the reaction shows no explosive characteristics makes a chain process doubtful. It was mentioned at the outset that Dixon and Higgins obtained lower ignition temperatures in nitrous oxide than in oxygen for most substances. This would naturally lead to the conclusion that oxidations by nitrous oxide would occur at temperatures comparable with those at which the oxidations by oxygen take place. This, however, does not seem to be the case. In addition to the present investigation and that of Melville with hydrogen, it has also been found that ethylene and acetaldehyde (9) do not react appreciably until high temperatures are reached. It may therefore be concluded that nitrous oxide is only effective as an oxidizing agent at temperatures approaching those at which its decomposition becomes appreciable.

SUMMARY

The reaction between gaseous methyl alcohol and nitrous oxide has been investigated from 500 to 570°C. The rate is very much greater than that of the thermal decomposition of nitrous oxide. The rate of reaction is approximately proportional to the concentration of nitrous oxide and independent of that of alcohol. The apparent heat of activation is about 60,000 calories per gram-molecule. The rate of reaction is proportional to the surface area, and the reaction is therefore either heterogeneous, or a

chain process in which the chains are initiated at the wall. The main reaction is probably

$$CH_3OH + N_2O = HCHO + H_2O + N_2$$
$$HCHO = H_2 + CO$$

We wish to express our indebtedness to the National Research Council of Canada for a fellowship awarded to one of us (R. D. McD.) during the tenure of which this work was performed.

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NOTE ON THE OXIDATION OF CINNAMALDEHYDE

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The oxidation of benzaldehyde to benzoic acid is known to proceed through the stage of the peroxide, but the final result is the simple addition of oxygen to form the acid. The oxidation of cinnamaldehyde probably proceeds through similar intermediate stages; it is slower than that of benzaldehyde, and the final result is more than the simple addition of oxygen according to the equation,

$$C_6H_5CH{:}CH{\cdot}CHO + \tfrac{1}{2}O_2 = C_6H_5CH{:}CH{\cdot}COOH \qquad (1)$$

Much more than this amount of oxygen was used up by the cinnamaldehyde in the authors' experiments. Also carbon dioxide was formed as the oxidation proceeded, the rate of production of the carbon dioxide increasing with the time. Approximately 0.2 volume of carbon dioxide was formed while 1 volume of oxygen was absorbed; and 1 g. of cinnamaldehyde absorbed 220 cc. of oxygen, though oxidation was still uncompleted. (According to equation 1, 1 g. of cinnamaldehyde forms 1.12 g. of cinnamic acid and absorbs 85 cc. of oxygen; all gas volumes in this paper are at N.T.P.)

Moreover formic acid vapor was smelt—and confirmed—after the oxidation of some cinnamaldehyde in a closed vessel. The smell of benzaldehyde also was noticed at the end of similar oxidations. Among the oxidation products of a large amount of the cinnamaldehyde were found formic, benzoic, and acetic acids, which were roughly estimated: 100 parts of cinnamaldehyde gave 107 parts of cinnamic acid (maximum value), 0.7 part of benzoic acid, 4.5 parts of formic acid, and 0.4 part of acetic acid.

This work must be regarded only as preliminary work indicating that the oxidation of cinnamaldehyde proceeds in a complex manner. Experiments are needed on the oxidation of pure (100 per cent) cinnamaldehyde in pure oxygen, dry and moist, with and without removal of the carbon dioxide as it is formed, and in the presence or absence of the other products of the oxidation. It may be mentioned that benzaldehyde has been detected when cinnamaldehyde is oxidized by potassium permanganate (solutions), both by the authors and by Nicholls (3), and by others; that

the accelerating effect of cinnamic acid on this oxidation is supported by the work of Almquist and Branch (1); and that acetic acid has been found in similar oxidations (2).

EXPERIMENTAL

The stock cinnamaldehyde, from Givaudan and Co., France, was colored yellow. The amount of cinnamic acid in this increased slowly from 4.5 to 7 per cent in three years. Some of the aldehyde was distilled in vacuo; after one such distillation the acid content was 2.0 per cent, and after a second distillation 0.85 per cent. All the acid figures quoted were found by titrations in alcoholic solution with carbonate-free caustic soda solution, using phenolphthalein, and the results were calculated as cinnamic acid.

Gasometric experiments

Cinnamaldehyde was dropped on to a filter paper placed at the closed end of a eudiometer, which had been filled previously with dry oxygen; the eudiometer was then inverted over mercury, some air being introduced in these operations. Then the volume of the gas was read during the following days and reduced to N.T.P. The first diminution of gas was rapid, but finality was long delayed. The volume of absorbed oxygen was greater than that calculated from equation 1. Also the titration of the final product indicated a quantity of acid which, assumed to be all cinnamic acid, should have resulted from a smaller volume of oxygen than that absorbed. Some typical experiments were as follows:

(1) The original aldehyde used (stock) = 0.1712 g. In this the acid content = 0.0099 g. Thus the net aldehyde = 0.1613 g. ≡ 13.7 cc. of oxygen, by equation 1. The original gas = 44.3 cc. (probably 80 per cent oxygen). The contraction equalled 14.2 cc. after 2 days, 18.7 cc. after 10 days, and 20.0 cc. after 19 days. The "contraction" may be low, owing to oxidation before the volume can be read at the start and to presence of carbon dioxide, here unmeasured. The acid formed by the oxidation, calculated as cinnamic acid, was 0.1513 g., which equals 11.5 cc. of oxygen (equation 1). In this experiment the oxygen was in excess.

(2) The original aldehyde (distilled) = 0.4241 g. In this the acid content = 0.0085 g. Thus the net aldehyde = 0.4156 g. ≡ 35.3 cc. of oxygen (equation 1). The original gas = 43.7 cc. The gas remaining was 11.9 cc. after 3 days, 12.2 cc. after 4 days, and 12.7 cc. after 7 days. The volume of 12.7 cc. consisted of 6.2 cc. of carbon dioxide and 6.5 cc. of nitrogen.

(3) An oxidation was carried out as above, except that samples of the gas were removed at intervals and were analyzed for oxygen and carbon dioxide. This experiment proved that the production of carbon dioxide

increased during the course of the oxidation. The first action is probably represented by equation 1, followed by side reactions.

(4) An experiment similar to experiment 2 was carried out with 0.355 g. of cinnamaldehyde spread over 0.2 g. of cinnamic acid in filter paper. This indicated a rather more rapid oxidation, reaching the same stage as the final stage of experiment 2 in 2 days. The presence of cinnamic acid therefore may accelerate the side reactions.

(5) An experiment similar to experiment 1 was carried out with benzaldehyde. The benzaldehyde used = 0.3734 g. In this the benzoic acid content = 0.0084 g. Thus the net benzaldehyde = 0.3650 g. ≡ 38.2 cc. of oxygen (equation 1). The contraction = 36.0 cc. after 1 day, and 36.1 cc. after 3 days. Titration of the final product indicated 0.3967 g. of benzoic acid, which corresponds to 36.4 cc. of oxygen. Benzaldehyde therefore oxidizes in the normal manner.

(6) In four experiments like experiment 2 the oxidation was started over mercury, and subsequently the carbon dioxide was removed by the introduction of caustic potash solution. The volumes of carbon dioxide produced per volume of oxygen absorbed were 0.166 (in 7 days, experiment 2), 0.198 (in 2 days, experiment 4), 0.213 and 0.225 (both in 6 days); mean value, 0.2. But this ratio of course will vary throughout the oxidation.

(7) This experiment was done with caustic potash solution over the mercury in the eudiometer throughout. The gas volumes were corrected for the vapor pressure of the caustic potash solution as well as for temperature and pressure; the temperature varied from 8°C. to 26°C., and the gas was kept, as usual, at about the atmospheric pressure, i.e., about 725 mm. The used cinnamaldehyde (distilled) = 0.2433 g. In this the acid content = 0.0019 g. Thus the net aldehyde = 0.2414 g. ≡ 20.5 cc. of oxygen. The gas volume was read over six months, and the following results are selected:

Time, in days	0	1	3	7	14	25	50	102	130	158	184
Contraction, or volume of gas absorbed, in cc.	0	18.5	24.7	31.9	36 9	41.5	44.4	47.9	49 6	50 65	51 4

The final ratio, $\frac{\text{Oxygen used}}{\text{Oxygen per equation 1}}$, is 2.51. In this experiment the oxygen was in excess throughout.

In a similar experiment the last ratio was 2.69 (over 190 days). This oxidation was probably completed; the final product had no smell of cinnamaldehyde, but it had a distinct smell of benzaldehyde.

(8) Similar gasometric blank experiments with the filter paper, in the presence or absence of cinnamic acid, and in oxygen either dry or over

caustic potash solution, showed no diminution in the volume of gas, i.e., no oxidation, for at least eighty days.

A large-scale oxidation

Cinnamaldehyde was placed in an open weighing bottle in a large vessel which was filled with dry oxygen. This aldehyde had been separated from the stock sample as bisulfite compound, regenerated, and distilled in vacuo; but it had been kept for twelve months in a desiccator before this experiment was started.

The original aldehyde = 20.94 g. In this the acid content = 1.54 g. Thus the net aldehyde = 19.40 g. In oxygen the gain in weight after 18 days = 0.42 g.; after 28 days = 0.54 g.; after 52 days = 0.98 g. In air the gain in weight after 74 days = 1.13 g. The total possible gain in weight according to equation 1 is 2.35 g.; in the experiment the oxidation is therefore about half completed. Also the gain of 1.13 g. corresponds to 10.45 g. of cinnamic acid according to equation 1. The

TABLE 1

Changes in the physical constants of cinnamaldehyde on oxidation

PER CENT CINNAMIC ACID IN THE ALDEHYDE	DENSITY	VISCOSITY	DENSITY	REFRACTIVE INDEX
5.20	1.0492	0.0470	—	—
5.78	1.0506	0.0486	—	—
0 9	—	—	1.055	1.6217
7.0	—	—	1.064	1.6207
13 9	—	—	—	1.6179

resulting acid crystals were separated from the liquid; the crystals weighed 8.7 g., and the liquid 13.4 g. As cinnamaldehyde saturated with cinnamic acid contains about 15 per cent of the latter, the liquid contains 2 g. of the acid, which therefore is the main product of the oxidation. The liquid was shaken with excess of caustic soda solution, and the emulsion was then shaken with ether. The aqueous layer was acidified, when 1.0 g. of aromatic acids was recovered; this product contained 5 per cent of benzoic acid, and the remainder was mostly cinnamic acid. The separated aqueous solution contained benzoic acid (0.01 g.), formic acid (0.4 g.), acetic acid (0.04 g.), and cinnamic acid (about 0.1 g. = saturated solution). The ethereal extract gave on distillation 8 g. of cinnamaldehyde and a higher boiling residue (aldehyde plus cinnamic acid plus any other products of oxidation and impurities). This residue was 1.3 g. Calling it cinnamic acid, the products accounted for were 11.1 g. of cinnamic acid, 0.06 g. of benzoic acid, 0.4 g. of formic acid, and 0.04 g.

of acetic acid, besides 8 g. of unchanged aldehyde; total = 19.6 g. The 22.1 g. of product thus would contain 9.1 g. of aldehyde, 12.5 g. of cinnamic acid, 0.07 g. of benzoic acid, 0.45 g. of formic acid, and 0.04 g. of acetic acid. Allowing for the acid in the original aldehyde and for the unchanged aldehyde, it was found therefore that 10.3 g. of aldehyde (net) oxidized to 11.0 g. of cinnamic acid, 0.07 g. of benzoic acid, 0.45 g. of formic acid, and 0.04 g. of acetic acid, besides the carbon dioxide found in the gasometric tests, and other probable products. There was found no oxalic acid among the oxidation products, and no formalin.

Benzoic acid was detected by the smell of ethyl benzoate and was estimated approximately by Nicholls' method (3). Acetic acid was detected by the smell of ethyl acetate and was estimated by distillation and titration and by afterwards checking the weight of the equivalent lead acetate. Formic acid was estimated by weighing the mercurous chloride reduced from mercuric chloride.

It was found that the crystals produced from the oxidation of cinnamaldehyde, although washed with benzene or carbon tetrachloride and subsequently dried for months in desiccators, only contained about 96 per cent cinnamic acid. Evidently small amounts of cinnamaldehyde become entangled and occluded in the crystals and final oxidation of these to acid is very slow. Melting-point determinations and a combustion analysis confirmed this supposition.

After titrating some oxidation crystals, which went 97 per cent cinnamic acid, the alcohol was distilled off, and the residue was extracted with ether. From the aqueous solution then the cinnamic acid was reprecipitated by adding hydrochloric acid; after washing well with water and drying in vacuo over sulfuric acid, the crystals analyzed 100.5 per cent cinnamic acid. Probably a trace of benzoic acid caused this high result.

As cinnamaldehyde oxidizes and holds more cinnamic acid in solution, the density and viscosity rise and the refractive index falls. Typical results are given in table 1.

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CHEMICAL ACTION IN THE GLOW DISCHARGE. XIV

The Ignition of Hydrogen–Oxygen Mixtures

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In previous papers (1, 2) the factors influencing the ignition of explosive mixtures of various gases in the condensed discharge were discussed in detail. The present communication describes a similar study of ignition in the positive column of the glow discharge. A $2H_2:O_2$ mixture was chosen for the study.

APPARATUS AND METHOD

The apparatus was the same as that described in the study of chain reactions in the positive column (3). In determining the conditions necessary for ignition, the discharge tube was first filled to the desired pressure, as read by a dibutyl phthalate manometer. The anode was lowered to exclude any positive column, and the discharge started at some low current. The anode was then raised until the desired length of positive column was introduced and the current was increased until ignition occurred, both the current and voltage being read at the instant of ignition. The fall of potential through the positive column was obtained by subtracting that for the negative glow from the potential drop between the electrodes.

RESULTS

The effect of pressure

The effect of pressure of the pure $2H_2:O_2$ mixture on the power input in the positive column for ignition is shown in table 1.

It will be observed that $(iV)\ P$ is constant to within the limits of experimental error. Thus the relationship between power input and pressure can be expressed in the form $(iV) = k/P$. This is in distinction to the condensed discharge, in which it was shown that $Q = k/P$, where Q is the quantity of electricity necessary for ignition.

The hyperbolic relation between power and pressure in the positive column is to be expected, from the fact that the heat developed as well as the number of active centers formed is proportional to the power expended.

In the condensed discharge, on the other hand, the spark jumps such a short distance that only part of the energy of the electron is dissipated in the gas; the production of active centers, therefore, is proportional to the number of electrons flowing rather than to the power.

TABLE 1

Effect of pressure of the mixture on the power input for ignition

P	$i \times 10^3$	V	$(iV)P$
mm. Hg	*amperes*	*volts*	
29.2	17.0	420	209
20.0	30.0	350	210
14.6	55.0	250	201

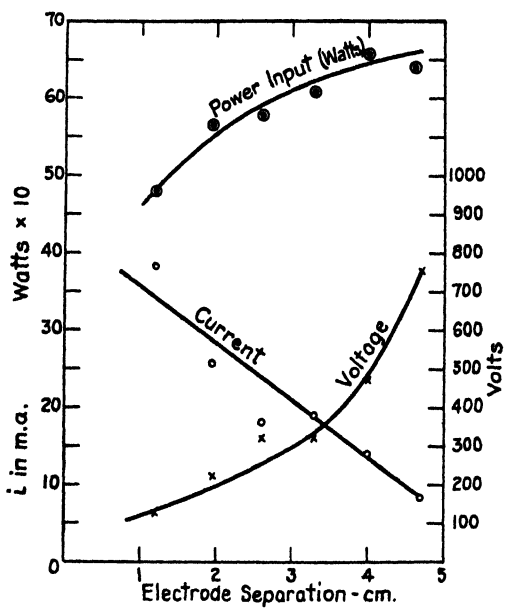

FIG. 1. THE EFFECT OF ELECTRODE SEPARATION

The effect of electrode separations

In figure 1 are given the current, potential drop through the positive column, and the power input at ignition for various separations.

It will be seen that while the ignition current decreases linearly with an increase in the electrode separation (d), the ignition voltage undergoes a rapid increase. The resultant power consumption increases only slowly with the length of the positive column, changing about 40 per cent for a

threefold increase in electrode separation. The propagation wave was set up at some place in the positive column and not at either of the electrodes; in so far as could be told the electrodes themselves had no direct effect on the ignition.

The effect of the $H_2:O_2$ *ratio*

The effect of varying the hydrogen: oxygen ratio at constant pressure on the power input for ignition is shown in figure 2.

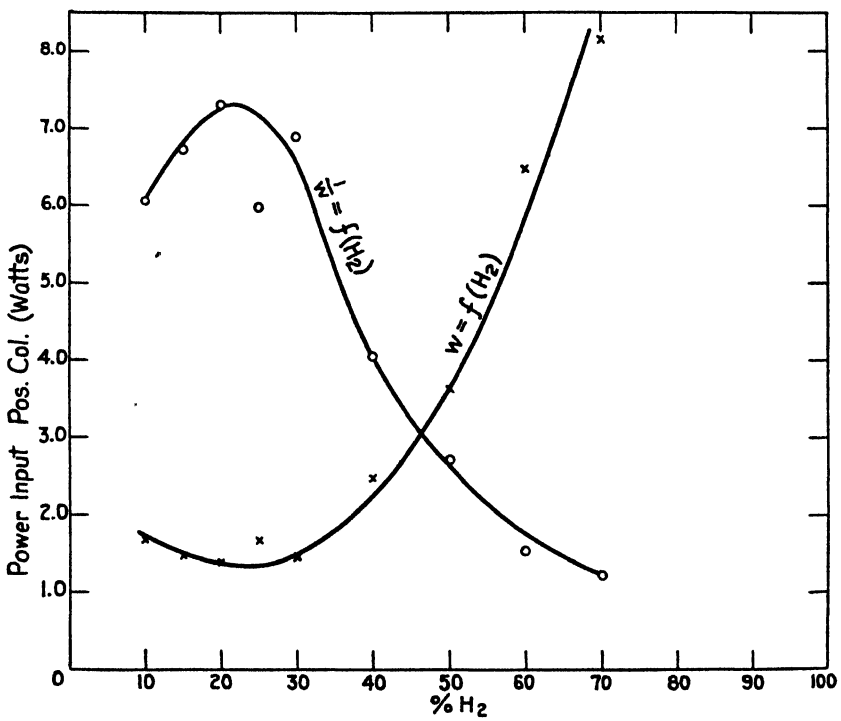

FIG. 2. THE EFFECT OF THE HYDROGEN–OXYGEN RATIO

The ignitability as given by $1/W$, and the power consumed, W, are both plotted. The power required for ignition reaches a minimum in a mixture containing 25 per cent hydrogen and 75 per cent oxygen; this power consumption is only 18 per cent of that required for the combining $2H_2:O_2$ mixture. This is in distinct contrast to the condensed discharge, in which excess oxygen had only a negligible effect on the quantity of electricity required for ignition.

The effect of added gases

The effect of various amounts of added gases on the power input for ignition is illustrated in figure 3. The partial pressure refers to the amount of gas added to 20 mm. of the $2H_2:O_2$ mixture.

The data show that the addition of hydrogen and helium to the explosive mixture results in an increase in the power for ignition, while water vapor, argon, nitrogen, oxygen, and nitrous oxide lower the explosive limit in the order named. The curves for oxygen and nitrous oxide were not symmetrical, owing primarily to changes they produced in the character of the positive column. Since the total pressure in the discharge was increased

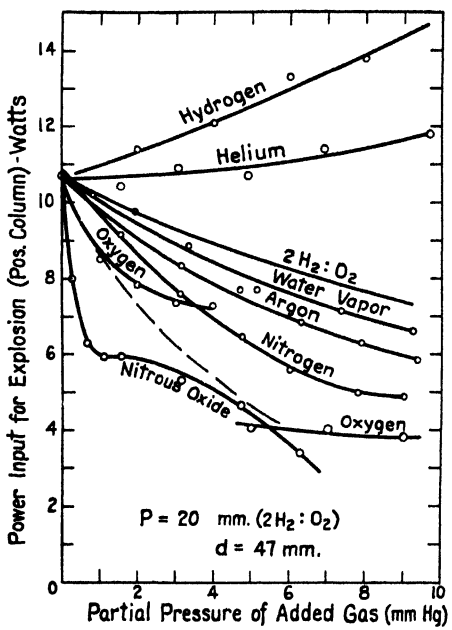

FIG. 3. THE EFFECT OF ADDED GASES

when the gas was added, the relative effects of these gases must be determined by a comparison with the $2H_2:O_2$ curve and not with the power input at 20 mm.

It will be observed that the order in which the various gases affect the ignitability is the same as that in which they affected the rate of reaction in the positive column for currents below that of ignition (3). The order is distinctly different from the effect of foreign gases on the rate in the negative glow (4). Likewise it is not at all the same as that found for ignition in the condensed discharge (2), where the order was more like that found in the negative glow, in that the ignition energy was lowered by hydrogen

and raised by most other gases in accordance with the complexity of their molecules. The order is slightly different from that found by Hinshelwood and Gibson (5) for thermal ignition where the gases are placed $H_2O > A > N_2 > He$.

The effect of glass walls

The presence of surfaces in close proximity to the positive column increased markedly the power necessary for ignition, whereas such surfaces several centimeters removed from the path of the discharge had no effect. The power input for ignition was substantially the same in 1-, 3-, and 5-liter reaction chambers. In the case of a discharge between two aluminum rods 5 mm. long and 2 cm. apart, ignition occurred for the same power input when a glass cylinder 2.7 cm. long and 3.2 cm. in diameter was surrounding the discharge as when it was absent; the axis of the cylinder was placed perpendicular to the discharge. (In these tests the axis of the discharge was horizontal.) On the other hand, when the cylinder was replaced by a glass rectangle 1 cm. wide, 3.8 cm. long, and 3.2 cm. high, ignition could not be induced with the power available, which was over twice that used for the cylinder. When the cylinder was placed parallel to the direction of the positive column, the axis of both being vertical, the effect was much more pronounced; the gas could not be ignited with the available power input without adding excess oxygen to the explosive mixture.

The effect of the surface material was studied by surrounding the positive column with a concentric glass cylinder 1 in. long and $1\frac{1}{8}$ in. in diameter, the cylinder being used both clear and heavily plated with silver on the inside. The diameter of this cylinder was sufficiently large to produce no effect on the power required to ignite the gas by a condensed discharge. The gas mixture chosen for the test was composed of one part of hydrogen and two parts of oxygen. The excess oxygen and the silver were chosen to test the effect of a possible production of ozone on the ease of ignition. The results showed that ignition occurred with 38 per cent smaller power input for silver than for the glass cylinder.

The effect of temperature

The ignition power input for various temperatures of the furnace surrounding the discharge tube is shown in figure 4.

These experiments were carried out at constant gas density, the pressure at room temperature being 20 cm. on the dibutyl phthalate manometer, which is equivalent to 1.54 cm. of mercury.

The data show that while the potential drop through the positive column increased somewhat with temperature, the actual power input for ignition decreased 8.75 times in raising the temperature from 300°K. to 600°K.

DISCUSSION OF RESULTS

The data just presented show that ignition in the positive column is distinctly different from that in the condensed discharge, in respect to the manner in which the ignitability is affected by the hydrogen:oxygen ratio, the presence of foreign gases, and the gas pressure. There is, however, a distinct analogy between the rate of reaction in the negative glow and ignition in the condensed discharge.

In the preceding article of this series a chain mechanism was developed which is adequate to account for the difference in reactivity in the positive column and in the negative glow (3). This mechanism involves two dis-

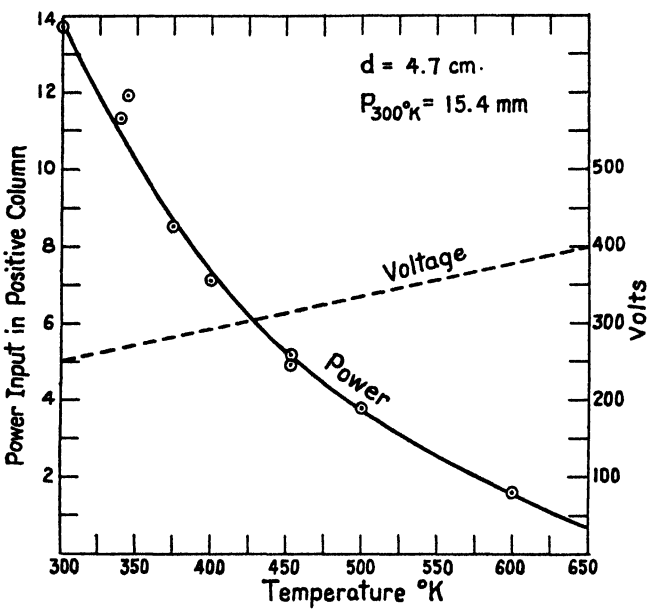

FIG. 4. THE EFFECT OF TEMPERATURE

tinct steps in the ignition process: first, the production of active centers; and second, the setting up of reaction chains about these centers. The important consideration in this mechanism is that for propagation to occur the active center must be in a gas of energy density such that it can receive its energy of activation, E, by collision with the energy-rich molecules through which it is moving. This condition can be brought about by the influx of energy from the outside (electrical, thermal, etc.), or by the heat liberated in the primary reaction about the active centers initially formed in the discharge.

This mechanism can now be used to account for the factors underlying ignition in the positive column, and for the differences found here and in

the condensed discharge. Obviously ignition is dependent on the conditions which favor chain growth. In the case of the effect of added gases, as shown in figure 3, it will be seen that the various gases decrease the power input for ignition in the order of their respective abilities to retard the rate of diffusion out of the discharge. This determines the order in which these gases increase the energy density in the path of the discharge, and thus increase the chance of the active centers receiving the activation energy, E, by collision with energy-rich molecules. Flame propagation, a condition in which the heat of reaction is capable of supplying the necessary activation energy, starts somewhere in the space occupied by the positive column, and is encouraged, therefore, by any condition which raises the energy density of this region. The curves illustrated in figure 3 are in general segments of hyperbolas, as is to be expected from the data in table 1. From this it follows that the effect produced by the added gases is proportional to the number of molecules in the path of the discharge.

In the case of the condensed discharge (2) foreign gases raise the power input for ignition in order of their ability to absorb energy from the discharge, the order being almost directly opposite to that observed in the positive column. In this case the energy is all introduced at one time and in a very small volume. Since the gas molecules surrounding this volume are in the normal state, active centers diffusing out are lost. For flame propagation to occur it is necessary that a quantity of gas burn in the path of the spark sufficient to produce the energy-rich molecules that supply the energy E requisite for the continuance of reaction chains; the problem, therefore, is one of the production of a necessary number of reaction centers. In consequence, the presence of a foreign gas which absorbs energy from the spark decreases the number of active centers, and hence necessitates a higher power input to burn the amount of gas required for propagation. Since the rate of reaction in the negative glow is proportional to the rate of production of active centers, it follows from the above considerations that the order in which various gases affect the rate must be the same as that in which they affect the ignition in the condensed discharge. It should be mentioned that while added gases also absorb energy in the positive column, this effect is necessarily small compared to the gain from the reaction chains made possible by the retardations in the rate of diffusion.

The importance of the energy density of the gas surrounding the region through which the discharge passes can be obtained by comparing the difference in the ignition energy per unit volume for the positive column and for the condensed discharge. An exact estimation cannot be made, but the order of magnitude can be obtained as follows: Referring to figure 1 it will be seen that about 50 watts is required for an electrode separation of 1 cm.; under these conditions the positive column is about 10 mm. in diameter and 5 mm. long, with a volume of about 400 cu. mm. The power

expended per cubic millimeter is 0.125 joule per second. In the condensed discharge at 1 cm. pressure, explosion occurs with 11 microfarads capacity at about 40 volts, the spark occupying not more than 1 cu. mm. of volume; the energy per cubic millimeter is 0.0098 joule. In the absence of inductance in the circuit the period of the discharge is between 10^{-4} and 10^{-5} seconds; this represents an expenditure of at least 98.0 joules per cubic millimeter per second. Since some energy is necessarily lost to the electrodes, a loss of as much as 50 per cent would still give an energy density four hundred times greater for the condensed discharge than for the positive column.

The effect of the energy density in the gas surrounding the discharge on the formation of reaction chains can be seen also from the various other factors influencing the ignition in the positive column. Thus, a twofold increase in the absolute temperature results in a ninefold decrease in the power input. Again, the power input per unit volume of positive column is decreased when the electrode separation is increased, as shown in figure 1. This would be very difficult to understand, since the ignition starts at localized points and not throughout the entire discharge at once, were it not for the fact that the energy flows from one segment of discharge into another, and thereby raises the energy density over that obtained from the power expended per unit volume alone; especially is this true in the present case where the axis of the discharge was vertical, so that the transfer of energy upward from lower portions of the discharge was aided by convection. The effect of surfaces near the discharge is also associated with the energy distribution. It is generally considered that reaction chains are broken upon contact with a surface. This, doubtless, accounts for the decrease in the reaction rate described in the previous communication (3), especially where propagation is possible. Walls surrounding the discharge break the chains, and, therefore, in limiting the reaction prevent the energy density from being raised to a point where ignition can take place. The fact that a silver surface lowers the ignition point less than does glass may be due to its ability to reflect the heat rays, thereby tending to raise the temperature of the gas in the path of the discharge.

SUMMARY

The factors influencing ignition in the positive column are contrasted with those obtained previously in the condensed discharge. Ignition does not occur in the negative glow, the N/H_2^+ ratio remaining almost constant irrespective of the pressure and power input.

The results show that the addition of foreign gases lowers the power input for ignition in accordance with the ability of these gases to retard the rate of diffusion; in the condensed discharge the order is almost the opposite, the work being increased in proportion to the amount of energy ab-

sorbed by the gas. The most easily ignited mixture of hydrogen and oxygen in the positive column is one containing 25 per cent hydrogen and 75 per cent oxygen.

A hyperbolic relation exists between power input for ignition and pressure.

The ignitability is increased ninefold for a twofold increase in temperature. It increases with the length of the positive column. It is decreased by the presence of surfaces near the discharge, but is unaffected by surfaces more than about 1 cm. removed.

The results are interpreted in the light of the cluster chain hypothesis presented in the preceding paper. The importance of the energy density of the gas surrounding the positive column is estimated by a comparison of the power input for ignition per unit volume of explosive mixture in the positive column and in the condensed discharge.

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PLATINUM ELECTRODE POTENTIALS IN MILDLY ALKALINE SUGAR SOLUTIONS, THE ELECTROMOTIVELY ACTIVE REDUCTANT PRESENT AND THE CATALYTIC EFFECT OF IRON ON ITS OXIDATION[1]

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It has long been recognized by those working in the field that platinum electrodes in alkaline sugar solutions do not acquire constant potentials which are so exactly reproducible as are observed on smooth electrodes in any of the reversible oxidation-reduction systems or on platinized platinum electrodes with hydrogen in the common buffers. Nevertheless, if conditions are carefully duplicated, the potentials are found to fall within a reasonably narrow range. They respond to the oxidation-reduction tendencies within the solutions. If a sufficient number of duplicate determinations be carried out, so that averages are significant, these electrode potentials can be made to yield considerable information concerning the complex equilibria existing in these solutions. This we have attempted to do and, in some thousands of experiments reported in this and previous papers (1, 3, 5), we have used more than a quarter of a ton of Merck's C.P. dextrose and a number of pounds of Bureau of Standards dextrose with which all findings were checked.

We shall consider first some of the reasons for the variability of platinum electrode potentials in sugar solutions at a pH not exceeding 10.5. Data will be given only for glucose. Other sugars, such as fructose, lactose, maltose, galactose, and sucrose, will, in general, yield qualitatively similar results. The cell, the potential of which was measured, was: platinum, sugar solution, saturated potassium chloride bridge, saturated calomel electrode. The temperature was kept at 30° ± 0.05°C. Unless otherwise stated, the apparatus and technic were the same as described in our previous paper (5).

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ADSORPTION EFFECTS

Clifton and Ort noted that for smooth platinum electrodes, which were in constant daily use and kept overnight in concentrated glucose solutions at pH 10, a simple rinsing with distilled water for the cleaning between runs resulted in the same potentials being registered by the electrodes as were observed following drastic treatment, such as standing in sulfuric and chromic acids, or in aqua regia, or heating to incandescence.

Tartar and McClain found that in certain solutions exposed to the air, smooth platinum electrodes had films adsorbed to them which extended a measurable distance out into the solution. Since many of our sugar solutions were made up exposed to the air, and since, even when air is carefully excluded, reducing sugars in alkaline solutions may attack the base or water to form oxygenated compounds, it was felt that adsorption of these oxygenated compounds of the sugars, or of oxygen itself, was the cause of the variability of platinum electrode potentials in these solutions.

A sugar solution was prepared, either by dissolving in the open air or by removing the oxygen from the buffer and electrode chamber with its dry sugar separately, by passing nitrogen through them for fifteen hours and then mixing them, precautions being taken to exclude the air at all stages of this process. When the electrode already in the chamber indicated the presence of a fairly strong reduction intensity, another similar electrode was heated to incandescence and, when cooled in the air for approximately fifteen seconds, so that it would no longer burn the finger if touched, it was plunged through a hole in the rubber stopper into the sugar solution, a particularly vigorous stream of nitrogen preventing entrance of any significant amount of air. The potential of this fresh electrode was then read at once and was invariably found to be considerably more reducing than the other electrode. However, the potential of the fresh electrode soon began to drift toward that of the other and, in time, both read approximately the same. For convenience, these electrodes will hereafter be designated respectively as "electrode No. 1" and "the fresh electrode." That these temporarily high negative potentials are not due to adsorption of any reducing gases from the flame during the heating to incandescence is shown by the potentials observed when the electrodes are plunged into a simple buffer solution which has previously been deoxidized. Here they always register, at first, a more positive potential than electrode No. 1, indicating that if any gas has been adsorbed it must have been oxygen.

A similar tendency of the fresh electrode to acquire more negative potentials than No. 1 electrode under these conditions was also noted in solutions of fructose, lactose, galactose, maltose, and sucrose, the difference between the potentials of the two electrodes being much less in solutions of fructose than in solutions of glucose and the other sugars studied.

Next, 0.1 cc. of a 30 per cent hydrogen peroxide solution was added to a

solution of 60 g. of glucose + 100 cc. of a buffer, which produced a solution of pH 9.00. Before the peroxide was added, No. 1 read −0.387 volt, and a fresh electrode read −0.482 volt. Five minutes after adding the peroxide, No. 1 read +0.307 volt, and a fresh electrode +0.349 volt. Here the fresh electrode was the more positive. From these experiments the conclusion is almost inescapable that adsorption of something on the electrode is preventing in the one case a reductant, and in the other case an oxidant, from registering on the electrode the potential that their concentrations and positions on the scale of oxidation-reduction intensities should produce. However, if much greater excesses of either hydrogen peroxide or potassium ferricyanide be added, so that several hours must elapse before the oxidant is reduced, then the fresh electrode, at the instant it is introduced into the solution, will register a potential only a little less positive than that which No. 1 is showing and will rapidly drift toward the latter value. The presence of appreciable amounts of hydrogen or other fairly powerful reductants will also make the two kinds of electrodes register the same.

Thus, the adsorbed material which is preventing electrode No. 1 from acquiring potentials representative of the concentrations of reductant and oxidant existing throughout the body of the liquid, can be removed at least partially from the electrode either by reduction or oxidation. This may be a compound of oxygen and glucose which can be represented as GO, or, since the solution is alkaline, as GO^-. Its reduction may or may not yield the original glucose, but it does eliminate the strong tendency to adsorb on platinum.

Electrodes which had been for some time in equilibrium with mildly alkaline glucose solutions, were removed from the solution and waved for a few moments in the air. The still moist electrodes were then returned to the glucose solution and at once registered a more negative potential than they had before this removal. Apparently the oxygen of the air had reacted with the adsorbed compound and lowered its tendency to stick to the platinum. The adsorbed material, in view of these observations, could hardly have been oxygen itself. If such an electrode is rinsed well with distilled water and again introduced into the sugar solution, the potential becomes still more negative, approaching that of a freshly ignited electrode. We believe that in both these manipulations the adsorbed GO^- is converted at the surface of the platinum to GO_2^-, which is then easily removed, leaving a "clean" surface of metallic platinum which, for an instant, responds to the active reductant present in an unmodified manner. Adsorption of the GO^- ever present in these solutions at once begins and, with its greater local concentration of GO^-, gives a drift toward more positive potentials.

It has been previously noted (3) that under the proper conditions the addition of hydrogen peroxide to alkaline glucose solutions is followed by

the formation therein of something intensely oxidizing. The oxidation potential goes up as high as +0.5 volt and more, which is more positive than can be observed with any concentration of pure hydrogen peroxide alone. We believe this high positive potential to be indicative of the presence of a glucose peroxide GO_2^-. Under these conditions the oxidation-reduction system, as far as the glucose is concerned, is $GO^- \rightleftarrows GO_2^-$. The coëxistence of any appreciable amounts of active reductant and GO_2^- would be impossible. The GO_2^- would be reduced by the active reductant almost the instant that the latter appears.

If oxygen be bubbled through such a solution at a rate to keep down the concentration of active reductant, small amounts of GO_2^- may be formed, at least momentarily, if another reductant is present which can be oxidized more easily by GO_2^- than by molecular oxygen. Shaffer and Harned have reported several such reactions and have assumed that in the oxidation of glucose there is formed first an oxide GO and then a peroxide GO_2, although they could get no direct evidence as to its existence.

It should be emphasized that these adsorption effects do not invalidate the determinations of the amount of active reductant present as carried out by Clifton and Ort. In those electrometric titrations the end point was determined by a jump in the peak potentials to more positive values, which indicated the momentary disappearance of all appreciable amounts of active reductant in the solutions. The actual potentials as read did not enter into the computation of the amount of reductant titrated. Neither does the adsorption interfere in the measurements of the rate of formation of the active reductant as carried out by Roepke and Ort, for, in making those measurements, large amounts of oxidant were added so that the solutions were kept strongly oxidizing for hours. Under these conditions, as mentioned before, we found no adsorption effects.

THE ELECTROMOTIVELY ACTIVE REDUCTANT

As stated in our former paper (5), we felt, because of the results of many other workers, that we had measured, in the case of glucose, the rate of formation of the 1, 2-enediol. However, as reactive as this form must be, it cannot exist long without undergoing chemical change. The electromotively active reductant, which accumulates even to the slight extent determined by Clifton and Ort, may not necessarily be this enediol form, through which stage the sugar may pass almost instantaneously.

An electrode was made by sealing a No. 18 platinum wire in the end of a glass tube and allowing it to protrude 1 mm. therefrom. Another electrode exactly like this was made, except that the exposed length of the wire was about 3.5 feet. Both were placed in the same electrode chamber in a solution of 60 g. of glucose +100 cc. buffer at pH 10.00, which was deoxidized by a stream of nitrogen. Both registered approximately the

same reduction potential and, on titrating electrometrically according to the technic of Clifton and Ort, both gave the same end point at around 2.5×10^{-6} gram-equivalents of electromotively active reductant. Yet the exposed surface of platinum was one thousand times greater in the longer electrode.

Pin point electrodes, with the platinum surface polished off even with the fused end of the glass tube, gave somewhat more negative potentials; platinized platinum electrodes gave potentials that were still more negative. However, our standard No. 18 platinum wire electrodes of about 45 mm. in exposed length, such as we have used in all our recent work, when immersed in a solution with a platinized electrode in it, still registered the usual potential and gave the same titration end point, showing that contact with the platinized platinum electrode did not greatly modify the solution generally, once the solution reached equilibrium.

TABLE 1

Measurement of potentials

60 g. glucose; 100 cc. buffer at 30°C.

pH	PLATINIZED PLATINUM ELECTRODE POTENTIALS		SMOOTH PLATINUM ELECTRODE POTENTIALS	
	H_2 pressure 1 atmosphere	N_2 gas passed in at 1 atmosphere pressure	Momentary values	Acquired values
7 07	−0.425	−0.364	−0 340	−0.100
7.98	−0.480	−0.428	−0 415	−0 227
8 98	−0 540	−0 500	−0 481	−0 313
10 00	−0.601	−0 570	−0 529	−0 392

Table 1 shows the results of experiments done with platinized platinum electrodes and smooth platinum electrodes, such as we have already designated electrode No. 1 and fresh electrode.

Freshly prepared platinized electrodes were placed in glucose solutions just after the solutions had been made up in the open air, and nitrogen was passed in. The time necessary for these solutions to reach equilibrium in contact with the platinized electrodes is shorter than is required when smooth platinum electrodes are put into them. The potentials as registered became constant after several hours and reproducible to within 2 or 3 millivolts of the values indicated in the third column. When the nitrogen was then replaced by hydrogen, the ordinary hydrogen electrode potentials as recorded in the second column were obtained. Therefore, in the absence of any added hydrogen these electrodes, which readily reach equilibrium with molecular hydrogen, indicated potentials in these sugar solutions corresponding to hydrogen at 9.3×10^{-3} atmospheric pressure

at pH 7, to 1.9×10^{-2} atmospheres at pH 8, to 4.7×10^{-2} atmospheres at pH 9, and 9.3×10^{-2} atmospheres at pH 10.

Other glucose solutions were prepared by deoxidizing the buffer and electrode chamber with the dry sugar in it separately with nitrogen for fifteen hours and then mixing out of contact with air. The potential on any platinum electrode in these solutions immediately after mixing is much lower than is found when this separate deoxidization is not done. After several hours, the comparatively steady potentials that No. 1 electrodes then registered were those recorded in the last column. These values can be duplicated with only rough approximation, since the time after solution is too short for the reducing sugar to reach completely the equilibrium that exists after from ten to fifteen hours. They are simply from selected individual experiments and must be compared with the simultaneous but momentary values of freshly ignited electrodes which are shown in the fourth column.

These fresh electrode potentials are usually reproducible to within 25 millivolts, or much less after the solution has stood for a somewhat longer time, or if the pH is around 9 and 10. They are "peak potentials," since the tendency of the electrode to reach equilibrium with the electromotively active reductant and to acquire a high negative potential is being opposed by the tendency of the electrode to adsorb GO^- and register a more positive potential. This latter process is more time-consuming, and hence, after a maximal reduction potential has been reached, a drift toward more positive values sets in. The platinized electrodes do not show this drift toward a more positive potential, but, if placed in the solutions soon after mixing and before the steady state is reached, they show a drift toward more negative potentials as the steady state is being set up. These platinized electrodes may catalyze at their surfaces some local reaction between the GO^- and the electromotively active reductant. Their potentials represent, then, maximal negative potentials which the peak values of the smooth fresh electrodes can never quite reach. These peak potentials correspond, in the case of pH 7 to 1.5×10^{-3} atmospheric pressure, of pH 8 to 6.9×10^{-3} atmospheres, of pH 9 to 1.1×10^{-2} atmospheres, and of pH 10 to 4.1×10^{-3} atmospheres of hydrogen.

We have emphasized the values for the partial pressures of hydrogen corresponding to these platinum electrode potentials because we feel that all the evidence is pointing to the conclusion that the electromotively active reductant accumulating to any appreciable extent in these sugar solutions, is actually molecular hydrogen. The partial pressures indicated are finite, although small. They correspond roughly in order of magnitude to the value of 2.5×10^{-6} equivalents of reductant for a solution similar to these at pH 10, as was determined by Clifton and Ort, and to a value of 1×10^{-5}, as has since been determined for pH 9 by the same technic. Data are not

available for the solubility of hydrogen in solutions such as these. Approximately 1.5×10^{-4} gram-equivalents of hydrogen at atmospheric pressure will dissolve in 100 cc. of water at 30°C., which is about the amount of water in our solutions. Therefore, at pH 10 there should be $\frac{2.5 \times 10^{-6}}{1.5 \times 10^{-4}}$ or 1.67×10^{-2} atmospheres of hydrogen in solution. The platinized platinum electrode indicated 9.3×10^{-2} atmospheres, and the peak value of the fresh, smooth platinum electrode 4.1×10^{-3} atmospheres. Similarly, at pH 9 the 10^{-5} gram-equivalents of reductant corresponds to a pressure of 6.6×10^{-2} atmospheres. At this pH the platinized platinum electrode indicated 4.7×10^{-2} atmospheres, and the fresh, smooth electrode 1.1×10^{-2} atmospheres.

The addition of platinized asbestos to a solution of 60 g. of glucose + 100 cc. of buffer at pH 10 caused an instant shift in the potential of the smooth platinum electrode previously in the solution toward a more negative value. When about 10 g. of 5 per cent platinized asbestos was added to such a solution, the smooth platinum electrode in it acquired practically the same potential as a hydrogen electrode in a similar glucose solution at that pH but without any platinized asbestos. Small bubbles of hydrogen sometimes appeared in the arms of the salt bridge. P. M. Horton has also reported the evolution of hydrogen gas from alkaline glucose solutions in which finely divided platinum was suspended, and M. H. Power has noted a tendency of platinum electrodes in alkaline glucose solutions to approach the potential of a hydrogen electrode.

We believe that this finely divided platinum removes the GO^- from the solution by adsorbing it on its surface. GO^- as a factor in a chain of equilibria producing both GO^- and hydrogen being thus removed, more hydrogen can accumulate until equilibrium is again established. If enough platinized asbestos is present, this removal of GO^-, and the consequent disturbance of the equilibria, can continue to an extent sufficient to build up temporarily the hydrogen concentration equal to that supported by a pressure of 1 atmosphere of hydrogen. The addition of a considerable amount of potassium ferricyanide to such a suspension causes electrodes therein to become strongly positively charged. After a preliminary period during which accumulated reductants are oxidized, the remainder of the oxidant is reduced at approximately the normal rate, showing that the finely divided platinum does not markedly catalyze the rate of formation of the enediol.

When a similar concentrated solution of glucose at pH 10 is evacuated, a smooth platinum electrode previously placed therein may show but little change, probably because diffusion cannot remove hydrogen faster than it is formed. If, however, such an evacuated solution be shaken, or a small amount of nitrogen be allowed to bubble through the solution, expanding

enormously thereby and violently agitating the solution, the electrode will, within a few minutes, become several tenths of a volt more positive. Similar shaking or the passage of a similar small amount of nitrogen through such a solution which is at atmospheric pressure, will produce comparatively little effect on the electrode potential. An extremely rapid stream of nitrogen at atmospheric pressure has been observed to change the electrode potential only about 7 millivolts. However, at pH 7 such a rapid stream passing through the solution at atmospheric pressure caused a shift in potential of 150 millivolts. Naturally the much smaller rate of formation will affect the net rate of removal by a gas in this manner. Similarly electrode potentials are more affected in this manner in dilute glucose than in concentrated solutions (4). These facts, taken together, show that a volatile reductant can be removed from these solutions by a vacuum or by the passage of a gas through the solution.

Finally if a solution of 60 g. of glucose + 100 cc. of a buffer to make the solution of pH 10 was placed in a 500 cc. distilling flask, which was then evacuated and sealed off from the vacuum pump, we found that after standing overnight, the gas which had collected over the solution could be pumped off by a liquid mercury pump and compressed into a small glass tube and measured. The amount of the gas thus collected, which was not water vapor, corresponded to a pressure of 1–2 thousandths of an atmosphere in the distilling flask. Pure oxygen was then admitted and mixed with this small amount of gas, and the mixture ignited by a glowing platinum wire. A contraction of one and one-half times the original volume of gas resulted. Confining the gas over a strong potassium hydroxide solution at any stage of the process did not change the results. We believe, then, that even mildly alkaline sugar solutions contain appreciable quantities of dissolved molecular hydrogen, which is in dynamic equilibrium with the sugars and their degradation products. It is the electromotively active reductant, the concentration of which is determined by the technic of Clifton and Ort.

OXIDATION AND ACCUMULATION OF HYDROGEN FOLLOWING THE ADDITION OF OXIDANTS

Clifton and Ort found that when oxygenated distilled water was added to glucose solutions at pH 10 in the absence of added iron, the peak potentials gave a curve similar to the solid line curve in figure 1. There was no end point. It seemed that the reaction, if any, between oxygen and the accumulated electromotively active reductant present was too slow, compared with the rate of formation of this reductant, to cause any sharp rise in potential when the amount of oxygen added just exceeded the amount of reductant present. This now seems reasonable, since molecular oxygen and hydrogen are rather inert toward one another.

When, however, a trace of iron was added, a curve, such as the solid line curve (figure 2) was obtained. We now believe that the iron catalyzed the reaction between oxygen and hydrogen under the conditions present in these solutions so that it sufficiently exceeded the speed with which hydrogen was formed, that any excess of oxygen present after all the hydrogen was destroyed would at once cause the electrode potentials to make a considerable jump toward more positive values. We believe that, in the presence of iron, oxygen can react rapidly with GO^- to form GO_2^-, and that the GO_2^- then rapidly oxidizes the hydrogen to form GO^- again and water.

Hence at pH 9 and 10 a detectable end point is possible, but not at 7 and 8 where the amount of accumulated hydrogen is too small.

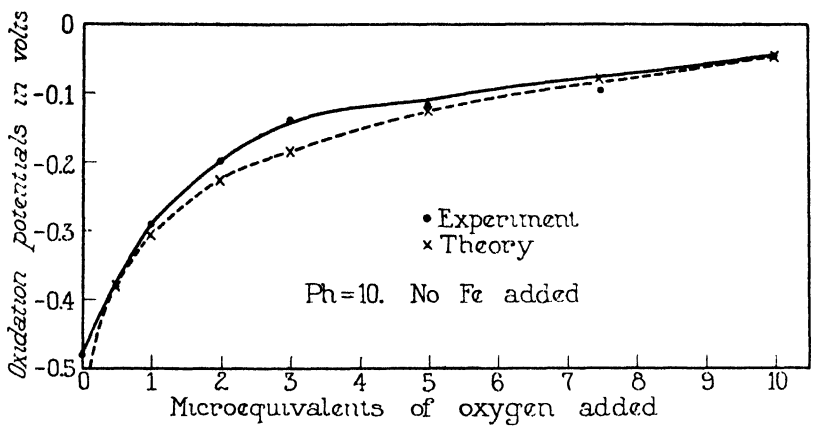

FIG. 1. PEAK POTENTIALS FOLLOWING THE ADDITION OF AERATED DISTILLED WATER

The time necessary to reach these peak potentials at pH 9 and 10 after the addition of the oxygen is never much longer than a few seconds, and often shorter depending on the amount of oxygen added. In fact, it could not be determined at all during a period of such rapid changing of the potentials, especially at pH 10, if it were not possible to set the potentiometer ahead of time approximately at the correct value as determined by previous trials. Very fast manipulation of the potentiometer is required then to determine the approximate peak potential, and the averages of many determinations were used to locate the points on our curves. We were aided somewhat by the fact that the most uncertain determination was the end point of our titration, which was just the point we were after. That is, for additions of lesser or greater amounts of oxygenated water, the voltage fluctuations near the peak voltages were much less in magnitude per unit of time. We also found it helpful to add the oxidant from a pipet carefully

to the top of the sugar solution until the pipet was emptied, and then to mix suddenly by a violent agitation of the solution with an unusually strong stream of nitrogen gas and by shaking the electrode vessel by hand.

We may assume that, in the absence of added iron, neither the concentration of hydrogen nor the adsorption of GO^- at the surface of the electrode has been appreciably affected during this short interval of time. Their effects on the electrode potential would therefore remain constant. In this case the peak potential would be proportional to the logarithm of the concentration of the added oxidant. This proportional relationship to the logarithm of the concentration of added oxidant follows from the well-known Nernst formulation stating that oxidation potentials are propor-

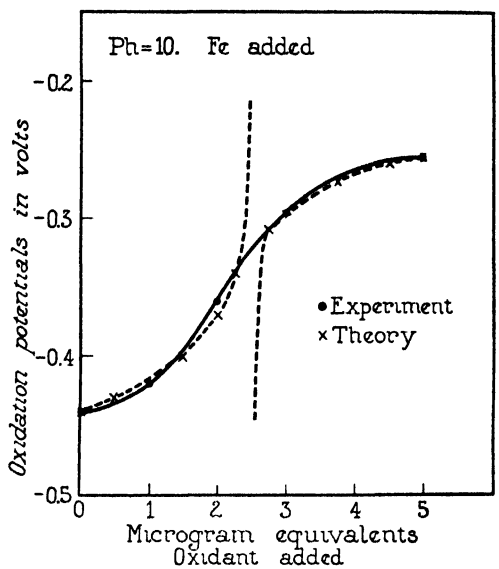

FIG. 2. PEAK POTENTIALS FOLLOWING THE ADDITION OF AERATED DISTILLED WATER

tional to the logarithm of the ratio of the concentrations of oxidant and reductant. Under these conditions the concentration of the reductant remains constant. When iron is present, and the indirect reaction between oxygen and hydrogen goes very fast, so that for the addition of only traces of oxygen there is an excess of hydrogen remaining and all the oxygen is gone, the potential should then be proportional to the logarithm of the amount of hydrogen in excess, since it is the only varying factor momentarily. When an excess of oxygen is added, and all the hydrogen is gone, the potential should be proportional to the logarithm of the amount of oxygen in excess.

In figures 1 and 2 the solid lines represent actual experimental data, the

averages of many single determinations. The dotted lines were plotted from points calculated on the foregoing assumptions. That is, the dotted line curve (figure 1) was constructed according to the equation:

$$P = P_0 - K \log_{10} X \tag{1}$$

where P = peak potential in volts as read after the addition of X units of oxygen, P_0 = potential when $X = 1$ unit, and K = proportionality constant. In calculating the points for the dotted line curve there are two constants, P_0 and K, to be evaluated, the values of which depend on the arbitrary choice of the value of a unit of added oxidant and for which two simultaneous equations are needed. To supply these the dotted line curve was made to coincide with the solid line curve at the potentials for 0.05 and 10 microequivalents of added oxygen. The broken line curves (figure 2) were also constructed from points calculated from the equation just given, as applied first to an excess of hydrogen and then to an excess of oxygen, X being first the excess of hydrogen, then the excess of oxygen. To construct the dotted line curve for an excess of hydrogen, the dotted line was made to coincide with the solid line curve at the potentials for 0 and 2.25 microgram-equivalents of added oxygen. For the excess of oxygen, the dotted line curve was made to coincide at 3 and 5 microgram-equivalents of added oxygen.

If we admit that in a mildly alkaline solution of glucose, kept out of contact with air, when the concentration of GO^- at the electrode surface is constant and there is no electromotively active oxidant other than GO^-, the potential of a smooth platinum electrode is proportional to the logarithm of the hydrogen concentration, and if we assume that a chemically reversible equilibrium exists between this hydrogen and certain derivatives of glucose, so that the reverse reaction or removal reactions prevent a large accumulation of hydrogen in solution, then it can be shown that the relation between potential and time after the reduction of added oxidants, may be formulated thus:

$$\frac{P^1 - P}{P_0 - P^1} = \frac{\log_{10}\left[e^{\frac{TR}{X_E}} - 1\right] - \log_{10} e^{\left(\frac{TR}{X_E}\right)}}{\log_{10} X_E} \tag{2}$$

and

$$T^1 = \frac{X_E \log_e F}{R} \tag{3}$$

where R = rate of formation of hydrogen, X_E = concentration of hydrogen at equilibrium, P = potential at time T, P_0 = potential for a concentration of hydrogen equal to unity, and P^1 = potential at equilibrium. T^1 =

time necessary for the concentration of hydrogen to be built up to a value so that $1/F$ = fraction of X_E yet to be accumulated.

It is obvious that the above equations will hold only for a period of time during which the electrode potential is proportional to the logarithm of the concentration of hydrogen. There must be no appreciable change in the GO^- concentration at the electrode surface. If an appreciable amount of hydrogen accumulates before the destruction of the last trace of any electromotively active oxidant which may be present other than GO^-, then

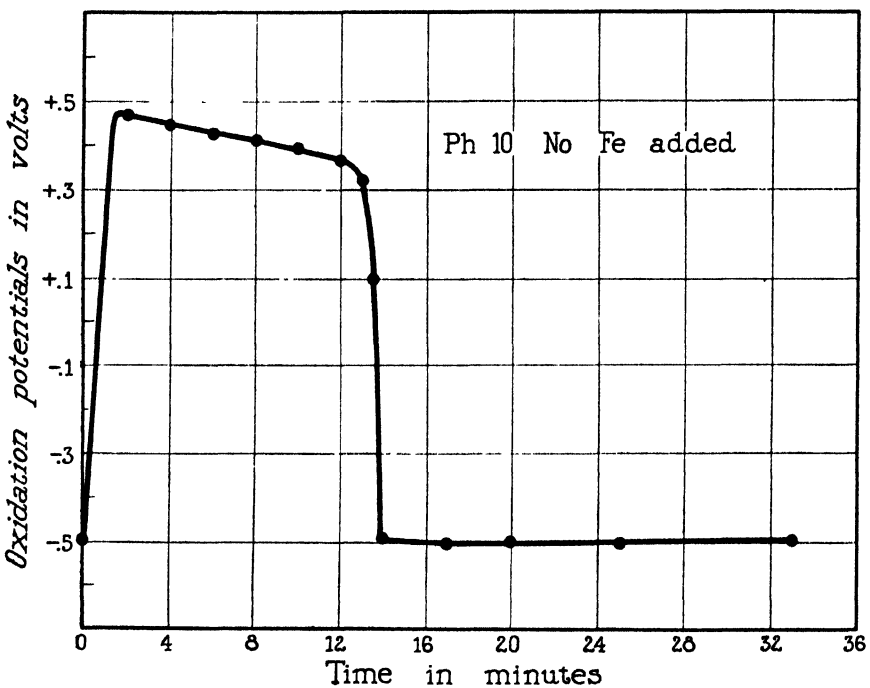

FIG. 3. DRIFT IN POTENTIALS FOLLOWING THE ADDITION OF POTASSIUM FERRICYANIDE

the equations will hold only after there is no significant amount of such oxidant remaining. Under such conditions the true zero time cannot be directly determined. But by taking several sets of time and potential values, after the oxidant is completely destroyed, enough simultaneous equations can be set up to calculate the equilibrium concentration of hydrogen.

At pH 10 the reactions are so rapid that the true zero time can be determined directly. Figure 3 shows the drift of potential following the addition of 0.002 gram-equivalent of potassium ferricyanide to a solution of 60

g. glucose + 100 cc. of buffer at pH 10. Thirteen cc. of $N/5$ sodium hydroxide was added with the potassium ferricyanide, which Roepke and Ort found was approximately sufficient to neutralize the acid formed during the reduction of the potassium ferricyanide. Therefore, just at the time the potential was dropping the fastest, the pH was fairly close to 10.

At pH 10, X_E was found by Clifton and Ort to be 2.5×10^{-6}, as indicated also by the point of inflection of the solid line curve of figure 2. R was found by Roepke and Ort to be 9.61×10^{-5} gram-equivalents per minute. Hence T^1 for X to equal $\frac{1}{2} X_E$ is 1.08 seconds. If so, the reaction at this pH should be too fast to permit a detailed checking of the formula by experimentally determined potentials. The curve in figure 3 shows that this is indeed the case, since the drop toward the equilibrium potentials is almost vertical. In taking the readings when the last trace of oxidant had disappeared at about the time represented by 13.5 minutes on this curve, the galvanometer went off scale in a flash, and a few seconds later, if preparations had been previously made, it could again be balanced at a potential around 0.6 volt more negative. Only an approximate titration end point, such as is determined by the technic of Clifton and Ort, is possible under these conditions at pH 10.

According to formula 3, using the values of Clifton and Ort and of Roepke and Ort, the equilibrium concentration for all practical purposes should be built up within ten seconds. It is seen that at this time the potential has indeed reached a value which is about the same as it had before any oxidant was added and near which it remains practically stationary for a number of minutes. This would indicate that the concentration of active reductant had again reached the value it had at the steady state before oxidant was added, and that the potential is indeed proportional to the logarithm of the concentration of hydrogen.

Since the agreement between the experimentally determined rate of potential fall after the reduction of potassium ferricyanide when added to these concentrated glucose solutions at pH 10 and the rate calculated from the above formulas is within the limits of experimental accuracy, the assumptions underlying the development of the formulas seem to be justified under these conditions. At lower values for pH and lower temperatures, where the rates of reaction are so much slower, it should be possible to check theory and experiment in more detail. Since such a check has been found to involve considerable discussion as to the chemical nature of the equilibria involved, this will be left to a subsequent paper. It is obvious of course that the above formulas will apply generally to any electrode potentials which are due to an electromotively active substance which is forming in solution at a steady rate and which in turn is disappearing from the solution at a rate dependent on its own concentration therein, so that ultimately a steady state is reached.

SUMMARY

Evidence has been presented which indicates that an oxygenated derivative of glucose, GO^-, adsorbs to the surface of smooth platinum electrodes and prevents them from acquiring the oxidation-reduction potentials which the concentrations and natures of the oxidants and reductants existing in mildly alkaline glucose solutions would otherwise impart to them. Such adsorption is believed to be the main factor in the recognized variability of the potentials on such electrodes.

Because of the conditions of the former experiments it is pointed out, however, that such adsorption was not an interfering factor in the work of Clifton and Ort in determining the concentration of electromotively active reductant, nor in that of Roepke and Ort in determining the rate of formation of this reductant.

Evidence is also described which indicates that the electromotively active reductant which accumulates to any appreciable extent in such solutions of glucose is molecular hydrogen. On the addition of an excess of oxidants, the hydrogen is oxidized, a glucose oxide, GO^-, is formed, and finally, under the proper conditions, a glucose peroxide, GO_2^-, exists which is electromotively active and gives high oxidation intensities. Finely divided platinum and iron do not affect the rate of formation of the active reductant in these sugar solutions, but do markedly catalyze the reaction between the sugar oxide GO^- and hydrogen and the reaction between these two and certain added oxidants. They activate the oxidants and GO^-, not the hydrogen.

A formula is given which expresses the relation between time and reduction potential following the reduction of added oxidants. It has been checked by experiment at pH 10. By the use of this formula and the rates of formation as determined by Roepke and Ort, the concentration of active reductant at equilibrium can be calculated if the equilibrium potential is known and the reduction potentials are determined at several intervals of time after the reduction of added oxidant is complete.

Although data are given in this paper only for glucose, these conclusions apply generally to many of the common sugars.

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THE HYDRATION OF THE CRYSTALLINE FIBERS OF SOAP CURD

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The commonest occurrence of soap is in the form of curd fibers embedded in a liquid crystalline solution, as in many household soaps. Some toilet soaps consist almost exclusively of curd fibers. These solid and concentrated forms of soap are the most difficult to characterize scientifically, and their nature is most open to dispute (5).

Curd fibers, by x-ray evidence (12, 13, 14, 15), are crystalline, exhibiting three spacings as distinguished from the one of liquid crystals. They have been shown to consist of hydrated neutral soap (4). They exhibit a definite solubility which is, however, very greatly dependent upon temperature and to a certain extent upon previous history. In our phase rule studies (6) we have found it possible to treat them as a phase or, rather, as a series of phases, although this is considered erroneous or incomprehensible by others.[2] This is partly due to the fibers not being massive; for although they may be centimeters long, they are finely microscopic or, more usually, ultramicroscopic in breadth and thickness. They thus present a large surface available for sorption, and all electrolytes are noticeably sorbed by them. Even saturated sodium chloride solution, which completely displaces other more dilute electrolytes from the curd fibers, does not prevent all non-electrolytes so far studied from being appreciably sorbed, glycerol being the sole exception.

One highly reproducible measurement has been made by four previous independent methods (3, 7, 9, 11). Sodium palmitate fibers at 90°C. in the presence of a saturated solution of sodium chloride are found to contain 2.1 mols of water to 1 mol of sodium palmitate. They also contain between 1 and 3 per cent of sodium chloride. Thus the strong negative sorption of sodium chloride by sodium palmitate is in reality a slight positive sorption by the hydrated fibers.

Using glycerol, Bennett (1) found that at room temperature the hydrated

[1] Experimental work carried out at Bristol University, England, in 1923–1927.

[2] For example, Ostwald and Erbring: Kolloidchem. Beihefte **31**, 345–46 (1930); however, they are doubtless depending upon their own assumption, "Da der Wassergehalt dieser Kernfasern zweifellos kontinuierlich variiert."

sodium palmitate fibers separating from ordinary isotropic (0.25 N_w) solution have the composition $NaP \cdot 10H_2O$, whereas those separating from more concentrated (1.0 N_w) anisotropic liquid solutions (liquide à conique) exhibit an empirical formula $NaP \cdot 4.3H_2O$.

The present communication employs the dew point method of measuring vapor pressure in studying the hydration of curd fibers of sodium palmitate and sodium laurate with and without the presence of a saturated solution of sodium oxalate. The results are unexpected in that they appear to indicate definite hydrates or amounts of water of crystallization.

EXPERIMENTAL METHOD

The dew point apparatus is that first designed by Cumming (2) with the essential modifications by McBain and Salmon (8) which convert it into a differential method. It is shown in diagram in figure 1.

A highly polished silver test tube is fitted with a rubber stopper in which is inserted a thermometer, reading to 0.01°C., and two glass tubes through which a rapid current of water is circulated by a power pump from and to a thermostat of adjustable temperature. The silver tube is held in a large rubber stopper fitted into an outer glass vessel which contains the close-fitting, thin-walled shell holding the solution or curd to be studied. The top of the outer vessel rises about one inch above the stopper, so that the closed space is completely immersed in distilled water in the transparent thermostat. A glass capillary tube, sealed to a stopcock, passes through the stopper holding the silver tube and may be connected with a water pump and the outer vessel thus evacuated if required. The glass outer vessel should be as small as possible so that equilibrium can be quickly attained.

The silver tube should be kept highly polished by a silversmith. Hand polishing requires practice. The motion should be along the length of the tube so as to avoid any disturbing transverse scratches. For cleaning, the tube was immersed overnight in freshly distilled thiophene-free benzene and lightly polished with silk which had been extracted with benzene. The effects of traces of hydrogen sulfide have to be removed by polishing with jeweler's rouge. The device of preventing formation of dew on a diagonal portion of the lower part of the silver test tube by coating it with an invisible film from boiling conductivity water was used in the manner originated by McBain. Illumination has to be carefully adjusted for optimum visibility of the boundary between the bright surface and that dimmed by incipient formation of dew. Too much dew may necessitate recleaning.

The silver tube was adjusted to 1.0°C. above the temperature of the thermostat before assembling as in figure 1. To hasten attainment of equilibrium the outer tube was evacuated. Under good conditions the difference between appearance and disappearance of dew was only 0.03°C.,

the mean being taken as the dew point. The zero correction, for differences between thermometers, and personal error, was found by one of us (H. I. B.), but not by previous workers, to depend slightly upon the condition of the silver tube, which was therefore subjected to an exact routine of cleaning and treatment. It is determined by measuring the dew point lowering of

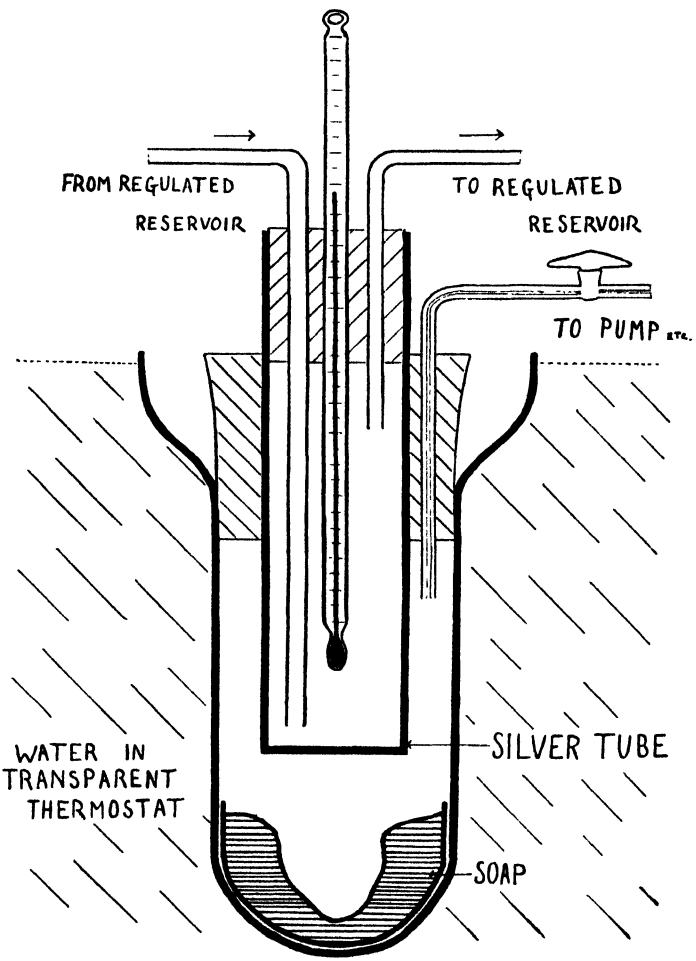

FIG. 1. DEW POINT APPARATUS FOR STUDYING VAPOR PRESSURE OF SOLUTIONS OR SOLIDS CONTAINING WATER

conductivity water itself; these measurements were repeated at frequent intervals as a check.

To insure avoidance of false equilibria with viscous solutions it is necessary to shake or stir the specimen being measured. With curds the most satisfactory device is to allow the curd to form in the vessel where practi-

cable and then to cut away the upper surface and the middle portion of the curd itself as shown in figure 1. Water diffuses better in this way than when the curd is a heap of separate lumps. The curd is allowed to remain in contact with the closed (evacuated) vapor space for several hours before taking a measurement. In the later experiments not more than 30 mg. of water was removed from a curd at a time; or, if large amounts were removed, the curd was left for a week in a closed vessel to recover internal equilibrium.

Dehydration of the curd within the dew point apparatus was found inadvisable and was rejected in favor of dehydrating the curd by placing its container in a vacuum desiccator and weighing from time to time. The chief disadvantage is that the exact composition at which a break occurs in the vapor pressure is missed and has to be surmised from inspection of the graphs of dew point lowering against gross composition of the curd.

The curds were subsequently analyzed by the methods and using the precautions described in previous communications. They were first dissolved in boiled-out neutral water, decomposed with excess of acid, the fatty acid titrated in 80 per cent alcohol, and the aqueous filtrate with standard alkali. Then if sodium oxalate was present, it was determined with permanganate.

A quicker method used in the later experiments on curds containing no oxalate was complete dehydration to constant weight. Thus with curd 25A (H. I. B.) complete analysis of 0.4232 g. of such completely dehydrated curd yielded 0.4230 g. of sodium palmitate. Thus from the weight at any time, the amount of water present was known by difference.

Each dew point lowering recorded is the mean of from six to twenty individual readings of which many thousand were required for the present work.

Results in presence of saturated sodium oxalate[3]

Sodium oxalate crystals were present in excess for the purpose of serving as an indicator to show when the last amount of free solution just evaporated. Up to this point the dew point has to remain constant, but thereafter any water withdrawn comes from the dry fibers of the hydrated soap curd and the vapor pressure falls suddenly.

The sodium palmitate and sodium laurate were special preparations made for us by Kahlbaum. They were dissolved by heating in a Jena glass-stoppered bottle at 90°C. until the solution was homogeneous. On cooling, a viscous pale yellow gel formed and became a solid white curd. After adding excess of Kahlbaum sodium oxalate, the solution was heated for twelve hours at 90°C., well shaken, and cooled to a solid white curd at 24°C. In some of these experiments the stirring or time allowed for equi-

[3] Experiments by L. S. S.

librium was insufficient, but the position of the break in the vapor pressure curve should be significant.

Dew point lowerings observed with saturated solutions of sodium chloride were 4.83, 4.84, 4.83, and 4.83°C. as compared with 4.82°C. in a mixture of solid salt and saturated solution. A similar mixture of sodium oxalate and saturated solution gave 1.46 and 1.45°C., which is therefore the constant reading to be expected until all water other than that actually held by the fibers is gone. The following results were obtained with the second specimen of soap curd, prepared from 0.5 N_w sodium palmitate containing excess of sodium oxalate:

Mols H_2O to 1NaP..	107	67	57	40	6	2.9	1.42	0 77	0 22
Dew point lowering, °C.	1 44	1 45	1 44	1 44	1 45	1 46	3.62	4 57	5 17

Other data from results with three other similar curds were:

Mols H_2O to 1 NaP	2 58	2 23	1 24	1.28
Dew point lowering, °C.	1 68	3 57	4 54	4.07

From the complete graphs for three curds the hydration of sodium palmitate fibers formed from 0.5 N_w solution containing excess of solid sodium oxalate was estimated as 2.52, 2.70, 2.58; mean, 2.6 mols H_2O to 1 mol sodium palmitate.

McBain and Salmon (9) obtained for the hydration of sodium palmitate prepared from 1.0 N_w solution in the presence of excess of sodium chloride the same result as that found here, namely, $NaP \cdot 2.60H_2O$, as compared with the value $NaP \cdot 2.16H_2O$ at 90°C. and $NaP \cdot 2.36H_2O$ at 50°C. Inspection of their table 1 for highly dehydrated curds shows that beyond the region of this break they too failed to obtain reproducible results; and all existing data for further dehydration are too uncertain to distinguish definitely between sorption, or a further definite hydrate, or both. We found by trial that a saturated solution of sodium oxalate may be made to yield only a fraction of its true dew point lowering by carefully avoiding any stirring. Water is forcibly abstracted to form the dew upon the silver; this is then returned to the surface of the solution, rendering it dilute. Similarly, with dried curd the dew point lowering may not be nearly great enough or may be too great, depending upon which factor preponderates, this, or as in these experiments, insufficient time for internal equilibrium.

It seems possible that the real composition of these curds formed in the presence of the two saturated salts, whose dew point lowerings are 1.45 and 4.83°C. at 20°C. (and 6.49°C. at 90°C.), is really the definite hydrate $NaP \cdot 2H_2O$; and that the actual composition so often confirmed at 90°C., $NaP \cdot 2.1H_2O$, as well as that at 20°C., $2NaP \cdot 2.6H_2O$, is due to superimposed sorption. It will be noted in the sequel that the gross composition, $NaP \cdot 2.6H_2O$ at 20°C. has been observed again even in the absence of salt.

Sodium laurate proves, as expected, to be much less hydrated than sodium palmitate. The break in the horizontal vapor pressure curve, which is followed by a great lowering, leaves as a result of two imperfect series the composition of the curd as $NaL \cdot 1.2H_2O$. This is less than that found by McBain and Salmon at 90°C. in the presence of saturated sodium chloride, namely, $NaL \cdot 1.80H_2O$.

Results with sodium palmitate curds in the absence of salt[4]

In two preliminary experiments (by L. S. S.) on the dehydration of 0.5 N_w sodium palmitate curd at 23°C. it was found that the dew point observed was steadily lowered until at the composition just above $NaP \cdot 9H_2O$ there was a sudden break, followed by a much more rapid lowering of the

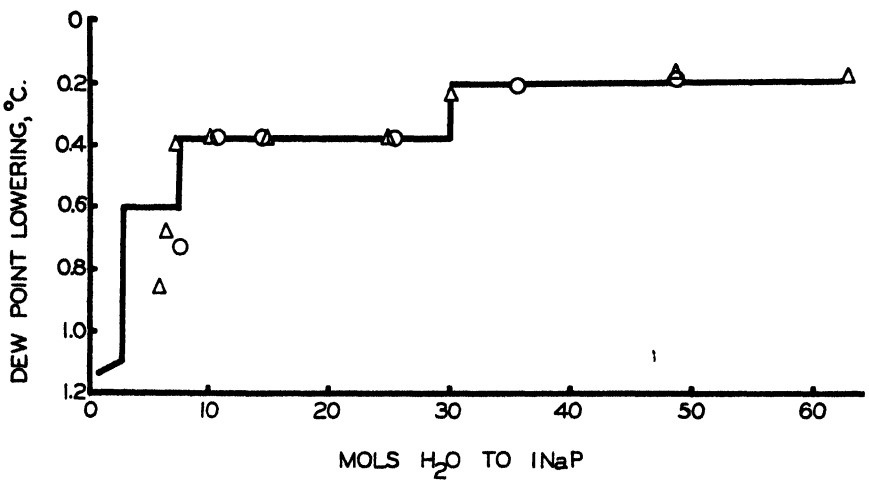

FIG. 2. DEW POINT LOWERING OF SOAP CURDS PLOTTED AGAINST GROSS COMPOSITION DURING PROGRESSIVE DEHYDRATION; CURD FORMED FROM 0.5 N_w SODIUM PALMITATE

dew point. This compares with the value $NaP \cdot 10H_2O$ found by Bennett at 20°C. from the negative sorption of glycerol in 0.25 N_w curd.

In developing the more careful technique required to follow up this result, one of us (H. I. B.) became convinced that the curves of vapor pressure against composition were essentially phase rule diagrams which consist of horizontal and vertical portions. As soon as exceptional care was taken in studying the vapor pressure of a particular curd, and much more opportunity was afforded for the attainment of equilibrium, the sloping curves of previous work were replaced by others such as are shown in figures 2, 3, and 4. In other words, soap curds appeared as definite hydrates of

[4] Experiments by H. I. B. except where otherwise noted.

definite composition and reproducible properties. The data seem fairly convincing, although this result was unexpected. It goes far beyond a mere demonstration that curd fibers contain bound water, a fact which was already established beyond peradventure even without the additional evidence given in both parts of this paper. Some way must be found for accounting, in the interpretation of x-ray data, for the water which is certainly present, perhaps through an arrangement of the water molecules on exposed surfaces.

The chief point at issue, after noting the fact of the presence of water in the dried fibers,[5] is as to whether the vapor pressure or dew point lowering curves are continuous, as in sorption, or discontinuous as in phase rule studies of definite hydrates, as drawn in figures 2 to 4. In the latter case

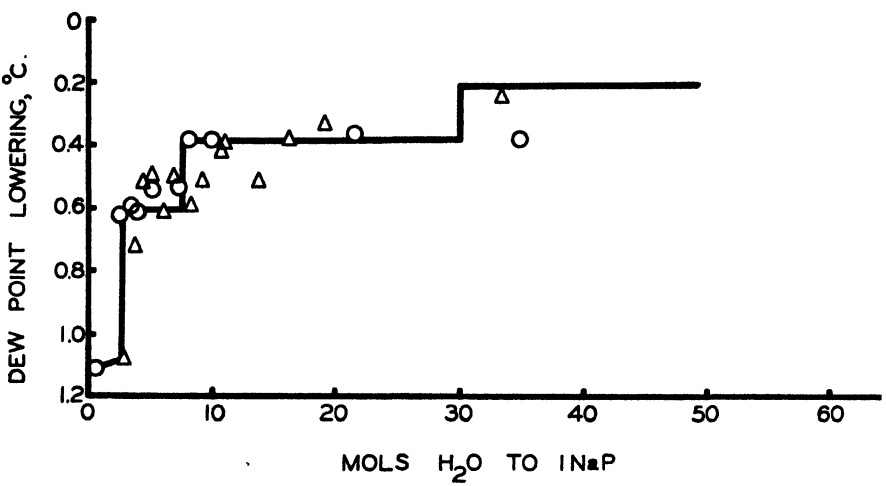

FIG. 3. DEW POINT LOWERING OF SOAP CURDS PLOTTED AGAINST GROSS COMPOSITION DURING PROGRESSIVE DEHYDRATION; CURD FORMED FROM 0.5 N_w SODIUM PALMITATE

the vapor pressure must remain constant until a hydrate has just been removed by dehydration, whereupon the horizontal line must drop to a new value as soon as again there are two solid phases in equilibrium with the vapor. The position of the break then gives the composition of the hydrate.

The first experiment was with 0.25 N_w curd of sodium palmitate at 20°C., showing a break at least at about $NaP \cdot 8H_2O$, although the curves are

[5] It will of course be noted that the dew point lowering corresponds to that of a highly concentrated solution, no such solution being present; the expressed mother liquor from the original wet curd being less than $N/50$, it was removed by the previous evaporation.

otherwise not definitive. The readings of gross composition and dew point were:

Mols H_2O to 1 NaP.. . .	102.3	77.5	43.3	19.3	13.7	8.6	7.3	6.6
Dew point lowering, °C...	0.19	0.18	0.25	0.30	0.31	0.31	0.47	0.60

The data for 0.5 N_w curds of sodium palmitate are given in figures 2 and 3, each of which records two independent series. The lines for all four are necessarily drawn in identical position in order to be consistent. They show a possible unproven break at $NaP \cdot 30H_2O$ and another undoubted one at $NaP \cdot 8H_2O$, or perhaps in one case nearer $NaP \cdot 10H_2O$. Only in the fourth experiment in figure 3, indicated by triangles, less reproducible results were obtained because the curd was employed, not in coherent

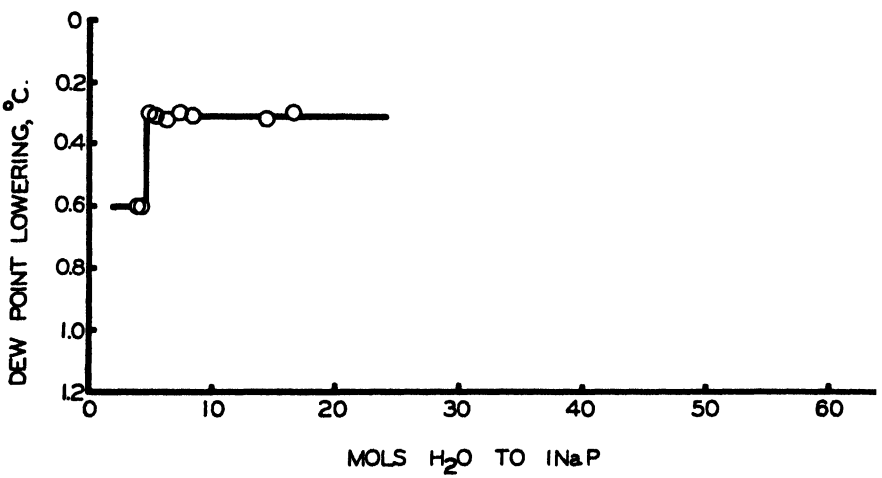

FIG. 4. DEW POINT LOWERING OF SOAP CURDS PLOTTED AGAINST GROSS COMPOSITION DURING PROGRESSIVE DEHYDRATION; CURD FORMED FROM 1.0 N_w SODIUM PALMITATE

form, but broken into pieces which did not come so readily into equilibrium. It is remarkable that in all cases the vapor pressure lowering of the dried curd between the compositions $NaP \cdot 30H_2O$ and $NaP \cdot 9H_2O$ is 0.38°C.

It seems also possible for one curve, studied sufficiently far, that the composition $NaP \cdot 2.6H_2O$ found in the earlier part of the paper corresponds to a break.

The whole point of figures 2, 3, and 4 is that, unexpectedly, they show breaks and that, furthermore, the position of the break for figures 2 and 3 at $NaP \cdot 8\text{–}10H_2O$ and the different one upon figure 4 agree with the hydrations previously published for these two different kinds of curd upon the basis of the method of indirect analysis. We can only repeat that these breaks, which we did not expect, have appeared only in those experiments in which the greatest care was taken to minimize false equilibrium.

Figures 2 and 3 for 0.5 N_w curds are in striking contrast to figure 4 for 1.0 N_w curd. Bennett had already proven by the glycerol method that for the former the curd had the composition $NaP \cdot 10H_2O$ and for the latter $NaP \cdot 4.3H_2O$, one having separated from isotropic soap solution and the other from liquid crystalline anisotropic smectic soap solution (liquide à conique).

The first experiment with 1.0 N_w sodium palmitate curd showed these to be still more difficult to study, but there was a break at $NaP \cdot 4.6H_2O$. The next and final experiment is that given in figure 4. The curd was allowed to dehydrate itself by being kept for some time in a fairly large closed vessel until it had lost not more than 0.02 g. between successive measurements. The dew point lowering is constant at 0.31°C. over a wide range of composition with a very definite break between $NaP \cdot 4.4H_2O$ and $NaP \cdot 4.9H_2O$. This is in excellent agreement with Bennett's wholly independent finding by the use of glycerol as a reference substance with analysis of exuded mother liquor.

We refrain in this place from discussion of the results obtained under the very different conditions at 90°C. on solutions of very different antecedents and properties. At 20°C. Bennett's results were based upon the assumption that no sorption occurred and that the concentration of glycerol in the expressed mother liquor was due solely to combined water within the curd fibers. However, if there is negative sorption of glycerol in the glycerol-curd fiber interface as there is in the glycerol-air interface, this could make Bennett's results slightly higher than the true hydration. The unique property of glycerol of not being sorbed by soap curd is not paralleled by its solubility in soap solution, for in unpublished experiments on partition between neat soap and lye it is found that the proportion of glycerol in the neat soap is several times that of any electrolytes present.

SUMMARY

The dew point method has been used at room temperature to demonstrate the presence of bound water in dried fibers of soap curd. When formed in the presence of a saturated solution of sodium oxalate, sodium palmitate fibers have the composition $NaP \cdot 2.6H_2O$. It would even appear possible that there are definite hydrates of sodium palmitate, including $NaP \cdot 8H_2O$ and, possibly, $NaP \cdot 2.6H_2O$ and $NaP \cdot 30H_2O$, although these results may be partially overlaid by sorbed water. Curd fibers obtained from liquid crystal anisotropic solutions contain half as much water as those from ordinary isotropic solutions. The behavior of soap curd, which is due to crystalline, although often ultramicroscopic, fibers, is wholly different from that of any gels or jellies.

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THE SYSTEM PYRIDINE–ACETIC ACID. II

Fusion Points

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INTRODUCTION

In a previous paper by one of the authors (10) the viscosities of pyridine–acetic acid mixtures were reported with a maximum viscosity for mixtures in the neighborhood of 80 mole per cent acetic acid. A similar behavior for this same system has been reported by Tsakalotos (11), Faust (5), and Dunstan (3).

While it is generally conceded that the existence of a maximum viscosity in mixtures indicates the formation of some type of compound or complex, it has been found that certain systems may show a maximum viscosity without compound formation between the components of the system. Further, it has been observed that the absence of a maximum viscosity does not necessarily indicate the absence of compounds (4).

In the viscosity data for the system pyridine–acetic acid, reported by Swearingen and Heck (10), it was shown that the maximum viscosity for the mixture in the neighborhood of 80 mole per cent acetic acid was quite pronounced at ordinary temperatures and was still very much in evidence at temperatures as high as 80°C. It was also shown that the composition at which this maximum viscosity appeared was practically independent of the temperature, remaining constant at about 80 mole per cent acid over the range of temperatures studied. In view of this rather peculiar behavior, the present authors have attempted to secure additional experimental data on this system, so that the nature of these mixtures having large viscosities may be more definitely characterized.

EXPERIMENTAL PROCEDURE AND DATA

The procedure adopted as most likely to give the desired information was to determine the melting point–composition relations for this system. The presence or absence of compounds in this system should be readily revealed by the melting point–composition diagram.

The theoretical basis and experimental technique of this procedure have been adequately discussed by Kendall (6). The melting point–composition relations do not always give a positive means of correlating compound

formation with abnormally great viscosities. Kurnakov, Krotkov, and Oksmann (7) find that some compounds are revealed on the melting point–composition diagram and not on the viscosity–composition diagram. The reverse of this case has also been found to be true. O'Conner (8) states that the fusion diagram fails to indicate compound formation in the system methylaniline–acetic acid, but that the considerable heat evolved on mixing these components indicates chemical combination. Further, Bramley (1) finds that the freezing point–composition diagrams for several phenols with certain organic acids do not indicate any equimolecular compounds, but he argues that they must exist.

A standard grade of glacial acetic acid was first repeatedly recrystallized and finally treated with phosphorus pentoxide and distilled under reduced pressure. A second quantity of the acid was purified by the method of Rüdorff (9). Both products showed a freezing point of 16.3°C.

A standard grade of pyridine was subjected to repeated fractional distillation, using a long Hempel fractionating column. The fraction finally collected for use boiled within a range of 0.5°C. This product was then allowed to stand over solid sodium hydroxide and then refractionated. The final product showed a melting point of −43.5°C.

From these purified materials, mixtures were made covering the entire range of composition. The compositions were expressed in mole per cent.

The freezing or melting temperatures were determined with either mercury or toluene thermometers, depending on the freezing points of the material under investigation. These thermometers were calibrated by means of a standard thermometer calibrated by the Bureau of Standards and by fixed points.

A small quantity of the mixture to be investigated was placed in a small closed glass tube along with the thermometer and stirring device. The tube was then placed in a freezing bath of solid carbon dioxide and ether, contained in a Dewar vessel. The mixture was frozen and the sample tube then removed from the freezing bath. The temperature of the sample was permitted to rise slowly, and the mixture was stirred uniformly after the first appearance of the liquid phase. The temperature at which the last small crystals disappeared was taken as the melting point of the sample. This procedure was repeated several times on each sample, the final melting points being quite reproducible.

The procedure, as outlined, was adopted after it was found that many of the mixtures exhibited a large degree of supercooling before crystallization could be induced. This condition was most marked in the region of high viscosity. In the case of samples of composition falling in the high viscosity range, in order to prevent the supercooled liquid from taking a glass-like "set," it was necessary to seed to induce crystallization. Similar conditions have been observed in other systems (2).

DISCUSSION OF EXPERIMENTAL RESULTS

The fusion diagram, figure 1, shows definitely the existence of two compounds and two eutectic mixtures. One eutectic mixture occurs at 30 mole per cent acetic acid with a melting point of −67.5°C.; the other at 66 mole per cent acid with a melting point of −59°C. One compound occurs at 50 mole per cent acid with a melting point of −48°C., corresponding to the simple salt, pyridonium acetate. The other compound has an incongruent melting point, above −42°C., as indicated by the extra-

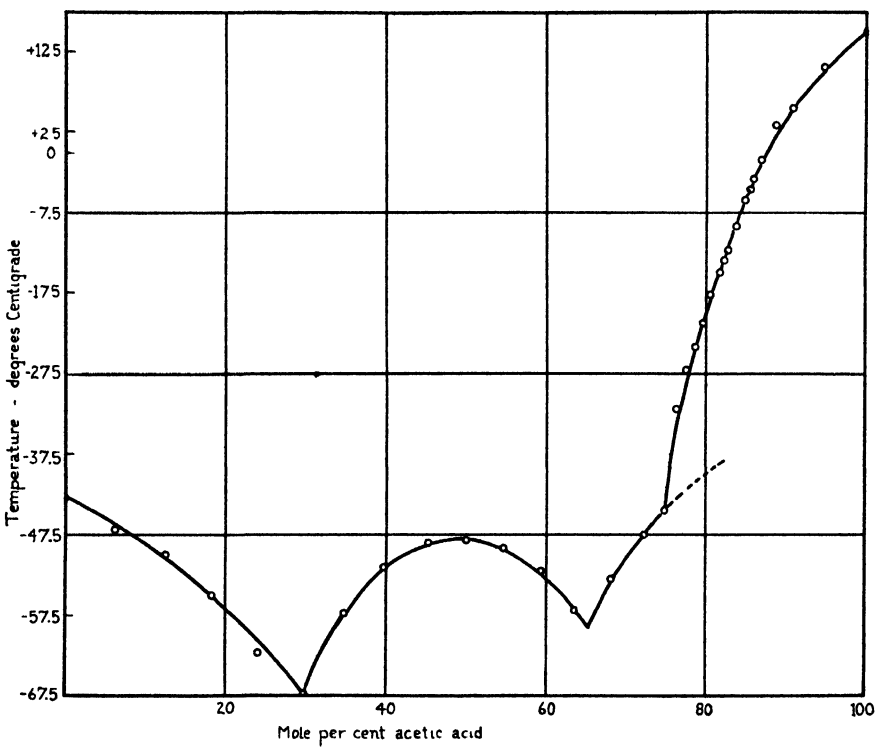

FIG. 1. MELTING POINT–COMPOSITION DIAGRAM FOR THE SYSTEM PYRIDINE–ACETIC ACID

polated (broken) line. The composition of this latter compound is probably either 80 or 83.3 mole per cent acid, since these compositions correspond to the compounds $C_6H_5N \cdot 4CH_3COOH$ and $C_6H_5N \cdot 5CH_3COOH$, respectively.

The compound melting in the neighborhood of −42°C. crystallizes from mixtures which fall in a very limited concentration range,—66 to 75 mole per cent acid. The fact that this compound is completely dissociated at temperatures above its melting point makes it seem highly improbable

that this compound, as such, is responsible for the maximum viscosity shown in this region. The abnormally high viscosity is still very much in evidence at temperatures considerably more than 100°C. above the melting point of this compound. No irregularity occurs in the viscosity–composition relation at the composition corresponding to the simple pyridonium acetate.

Thus, the melting point–composition diagram for this system indicates the existence of two compounds, one of which is indicated by the viscosity–composition relationship. While there is a certain degree of coincidence in the probable composition of this compound and the composition of the

TABLE 1

Melting points of pyridine–acetic acid mixtures

MOLE PER CENT ACETIC ACID	MELTING POINT	MOLE PER CENT ACETIC ACID	MELTING POINT
	degrees C.		*degrees C.*
0 000	−43 5	77.722	−26.9
6 345	−47.1	78.698	−23.8
12 566	−50.6	79 734	−20 9
18.529	−55.3	80.771	−17.7
24.359	−62.3	81.543	−14.7
29.943	−67.5	82.221	−13 3
35 225	−57.4	82 669	−11.9
40.268	−51.6	83.720	−9.2
45.440	−48.6	84.773	−5 8
50.004	−48.2	85.234	−4.5
54.890	−49 1	85.894	−3.0
59.594	−52.3	86.470	−0.6
63.927	−56.7	86.790	0 0
68.202	−52.9	88.568	3.7
72.438	−47.5	90.710	6.6
74.790	−44.5	94.834	10.95
76.256	−31.8	100.000	16.3

mixture having maximum viscosity, this cannot be due to the compound itself. The agreement may be accidental or may be due to some peculiarity of this dissociated compound. The fact that the simple stable compound formed has no noticeable effect on the viscosity of the system, indicates that compound formation is neither the necessary nor the sufficient condition for a maximum viscosity to occur.

SUMMARY

1. The melting points of various mixtures of pyridine and acetic acid have been determined and the melting point–composition diagram constructed.

2. The melting point–composition diagram for this system indicates the presence of two compounds, $C_6H_5N \cdot CH_3COOH$ and $C_6H_5N \cdot 4CH_3COOH$ (or $C_6H_5N \cdot 5CH_3COOH$), melting at −59°C. and about −42°C., respectively.

3. The simplest of these compounds revealed on the melting point diagram is not revealed on the viscosity–composition diagram. While the more complex compound is revealed on the viscosity–composition diagram, its responsibility for the maximum viscosity occurring here, is, to say the least, questionable.

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INTERPRETATION OF THE PRESSURE–VOLUME–TEMPERATURE RELATIONS OF SINGLE AND COMPOSITE GASES

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In a recent article (3) is given an equation which adequately describes the P–V–T relations of several important gases over a pressure range from 1 to 3000 atmospheres, and over a temperature range from 0°C. to 200°C. The purpose of the present article is to show that the equation is equally applicable to the P–V–T behavior of mixtures of those gases, and over a much greater temperature range. The results are presented in two condensed tables.

The data for hydrogen, the mixture of hydrogen and nitrogen, nitrogen, and carbon monoxide are taken from recent articles by Bartlett (2); those for carbon dioxide from Amagat (1). In order to economize on space all the original data are omitted, since they are easily accessible. The value of V_∞ for the 3 to 1 mixture of hydrogen and nitrogen gases was obtained from the additive relation,

$$1/V_\infty = 4/(3V_\infty \text{ of } H_2 + V_\infty \text{ of } N_2)$$

The value of V_∞ for carbon monoxide was read off on the curve $1/V$ vs. log P as described in the previous paper. In the case of carbon dioxide, however, the data do not extend sufficiently far to determine the point of inflection, as a glance at figure 2 will show. It was therefore found necessary to resort here to the less reliable method already mentioned (3), namely, the calculation of V_∞ from the density of the substance in its solid state. In the literature it is stated that the density of carbon dioxide "glass" is 1.56 at about 194° Absolute. From this value $1/V_\infty$ was found to be approximately 800.

DISCUSSION OF THE CONSTANCY OF K

In discussing the constancy of K in the given equation,

$$(V_1 - V_\infty)/(V - V_\infty) = P^K$$

it may be pointed out that a change in K of 0.1 per cent produces a deviation of about 0.4 per cent in the calculated volumes or densities of a given

gas. Hence, a 2 per cent or 3 per cent change in K would render the equation useless for interpolation or extrapolation purposes, provided there were a definite trend in the K values. If, however, the values of K varied more or less alternately to the extent of 2 per cent or 3 per cent, it would merely indicate large experimental errors, which might be inherent in the method of measurement. Thus the K values for hydrogen gas at 0°C. calculated from Amagat's data vary among themselves to the extent of 1 per cent, corresponding to a 4 per cent error in the original measurements; while in the K values from Bartlett's data, obtained presumably under like condi-

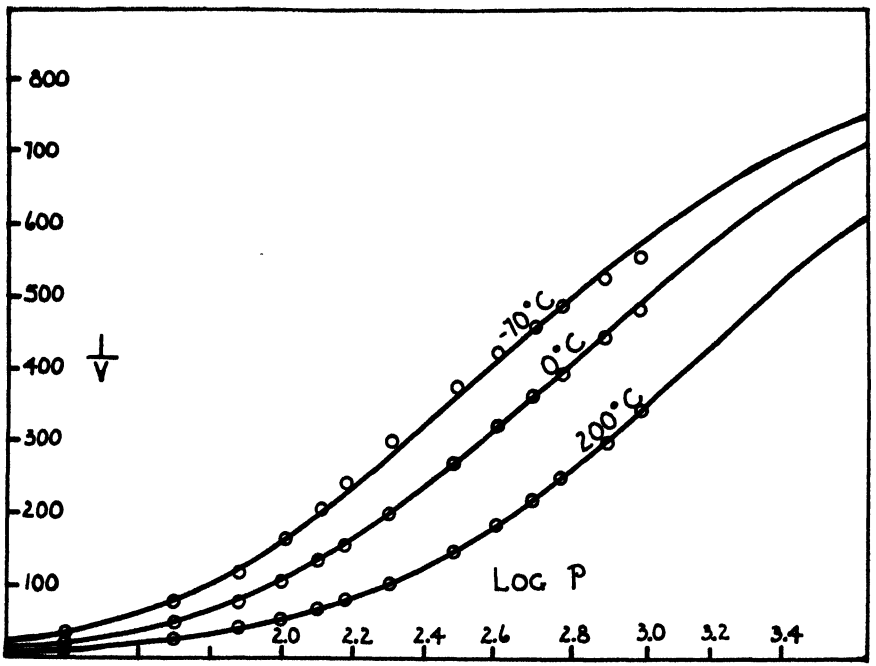

FIG. 1. P–V–T RELATIONS OF CARBON MONOXIDE GAS

tions, the largest deviation is only 0.1 per cent, corresponding to a maximum experimental deviation of only 0.4 per cent. In other words, Bartlett's results, in this case, appear to be ten times as accurate as the results of Amagat, yet each investigator claims the same degree of average accuracy, about 0.2 per cent; this is true for Bartlett's results, but not for those of Amagat. In this connection it may be mentioned that the ultimate molal volume for hydrogen gas calculated from Amagat's data is about 15 cc., while if calculated from Bartlett's data the ultimate molal volume is about 16 cc.; this value is used in the present calculation. Furthermore, the K values of hydrogen calculated from Bartlett's data indicate that

hydrogen, instead of being an exception as noted in the paper cited (3), behaves like all other gases; that is, the average K values for the different temperatures are never less than unity. It is also interesting to note that the K values increase with the molecular weight of the gas (see figure 3), approaching unity at high temperature for the several gases studied. This being the case, it follows that K cannot be less than unity, since hydrogen is, at present, the lightest of all gases.

In the case of nitrogen gas the experimental results from both sources seem to be of about the same degree of accuracy, namely, 2 per cent to 3

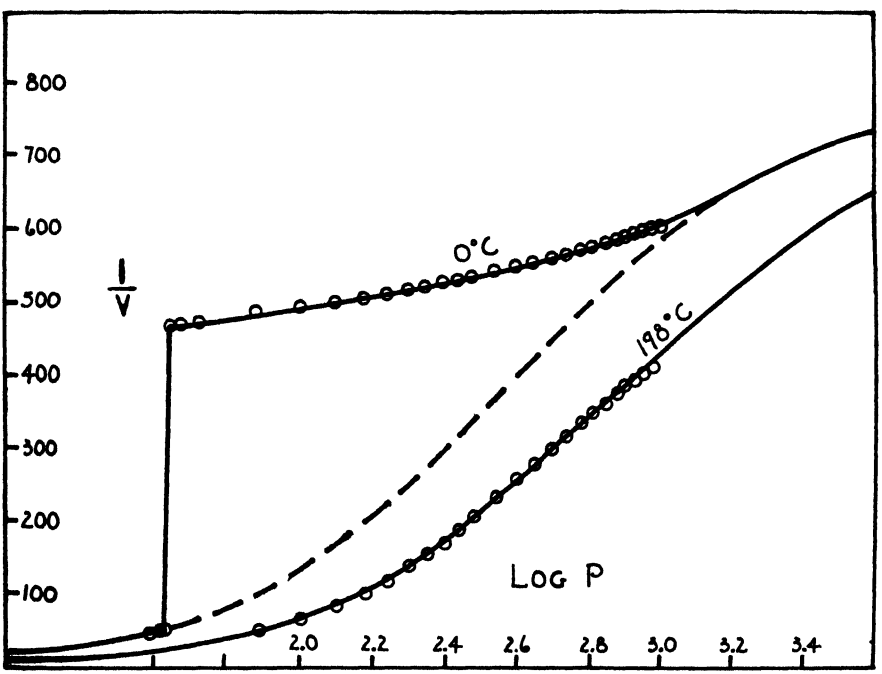

FIG. 2. P–V–T RELATIONS OF CARBON DIOXIDE GAS

per cent. The largest experimental deviations appear in Amagat's data for carbon dioxide gas; but the K values for this gas at 0°C. remain fairly constant up to the point of liquefaction of the gas, where the curve becomes discontinuous. At about 1000 atmospheres pressure the curve merges again into the calculated curve where the value of K is only slightly higher than the average. It is evident from a glance at the graph that if the data extended above 1000 atmospheres pressure the K values would regain their former constancy.

To obtain a comparative view of the experimental deviations for the several gases, the values calculated for −50°C. and for +50°C. seem suffi-

cient and representative. These are given in table 2. They were calculated from the equation,

$$(dC/C) = (C_\infty - C)/C_\infty(\log_e P)dK$$

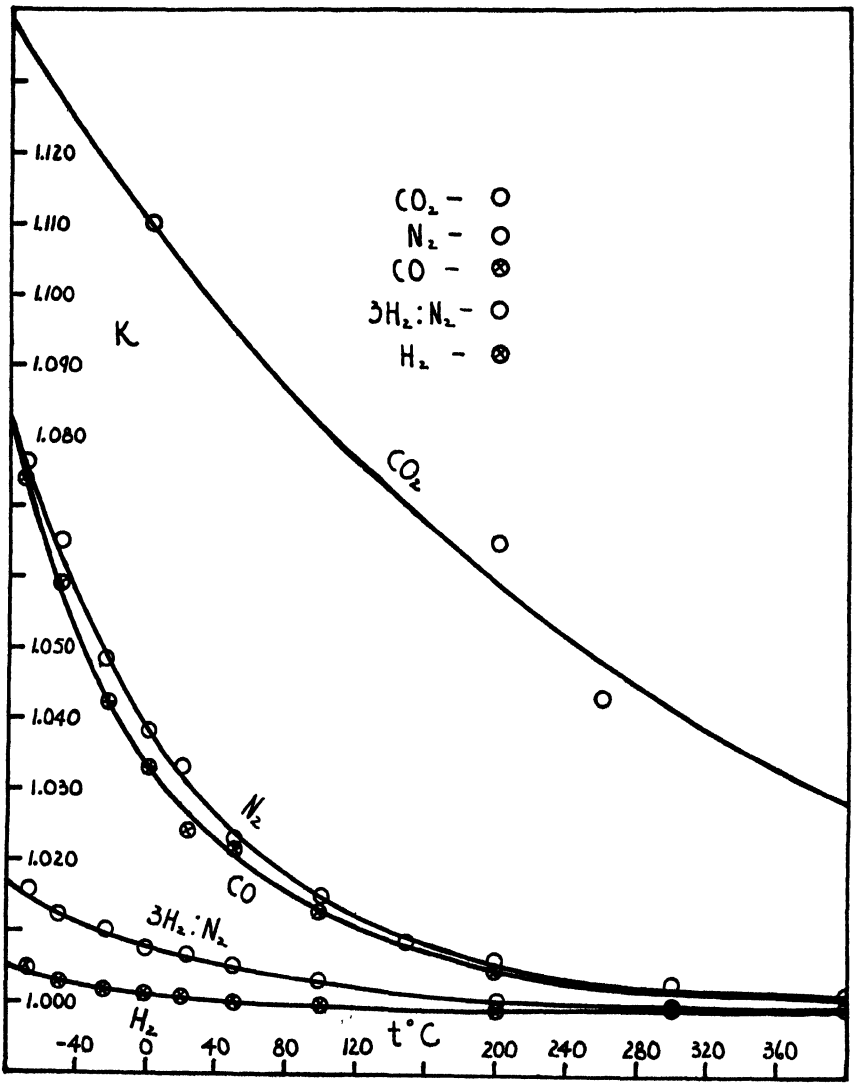

FIG. 3. RELATION OF K AND t

where C denotes the molal density (since the quantity of gas is always 1 mole, $C = 1/V$) of the gas at pressure P; C_∞, the ultimate molal density at infinite pressure; and dK, the difference between any value for K and the

arithmetic mean of a given series. The above equation is obtained by differentiating the original equation for a given pressure.

TABLE 1

Summary of the values of K

T	H_2		$3H_2:N_2$		N_2		CO		CO_2	
	K_m	K_r	K_m	K_r	K_m	K_r	K_m	K_r	K_m	K_r
degrees C.										
−70	1 004	1.002 1.006	1 015	1 012 1 020	1 076	1.049 1 102	1 073	1 031 1.110		
−50	1 003	1 001 1 004	1 012	1 005 1 016	1 065	1 042 1 079	1 060	1.022 1 083		
−25	1 002	1 001 1 003	1 101	1 004 1 012	1 048	1 035 1 060	1 042	1 015 1 060		
0	1.001	1 001 1.002	1 008	1.004 1 009	1.038	1 024 1 048	1 033	1.013 1 048	1 110	1 104 1 112
20	1 001	1 061 1 001			1 033	1 026 1 040				
25			1 007	1 003 1 008			1.024	1.010 1 038		
50	1 000	1.000 1 000	1 005	1.002 1 005	1 023	1.012 1 030	1 022	1.008 1 031		
100	1 000	1 000 1 000	1 004	1 002 1 004	1 015	1 007 1.020	1.013	1.005 1 020		
150							1 008	1 001 1 012		
200	1.000	0.999 1.000	1 001	1.000 1 001	1 006	1.002 1.008	1.005	1.000 1.008	1.065	1.029 1 081
300	1.000	0.999 1.000	1.000	1.000 1.000	1.003	1 002 1 004				
400	1.000	1.000 0.999			1.001	1.000 1 001				

All the deviations are calculated on the basis of four significant figures in the corresponding values for K, since 0.1 per cent variation in K is within the probable experimental error mentioned in the original articles cited above.

In conclusion it may be pointed out that the most concordant data are those of hydrogen gas by Bartlett, and the least concordant data are those for carbon dioxide gas by Amagat.

EXPLANATION OF THE TABLES

In table 1 is given a summary of the constants, where K_m denotes the arithmetic mean at a given temperature over the pressure range shown in column 1, table 2. Under K_r are given the largest and the smallest K values, or the range, of a given series. The other headings are self-explanatory. In table 2 are given the calculated deviations and the values for V_∞ of the several gases. The averages at the foot of table 2 were calculated without regard to the algebraic signs prefixed to the individual deviations. The values for the ultimate molal volumes are placed at the conclusion of table 2. The values for V_1, the molal volumes at 1 atmosphere pressure, may be found at the head of the columns marked PV in Bartlett's (2) original tables.

TABLE 2

Values of (dC/C)

P	H_2		$3H_2 \cdot N_2$		N_2		CO		CO_2
	−50°C.	+50°C.	−50°C.	+50°C.	−50°C	+50°C	−50°C.	+50°C.	+198°C
atmospheres									
25	+0.0063		+0.0220				+0 1053	+0.0349	
50	+0.0037	0.0000	+0.0186	+0.0113		+0 0409	+0.0649	+0.0297	
75	0.0000		+0.0120				+0.0114	+0.0160	
100	0 0000	0.0000	+0.0081	+0.0086	+0.0192	+0.0124	−0 0346	+0.0041	+0.0912
125	0.0000		0.0000		−0.0114		−0.0612	−0.0085	+0.0524
150	−0.0044		−0.0043		−0 0489		−0.0830	−0.0171	+0 0398
200	−0.0045	0.0000	−0.0130	+0.0046	−0.0506	−0.0170	−0.0985	−0.0300	0 0000
300	−0.0045	0.0000	−0.0170	0.0000	−0.0432	−0.0290	−0.0710	−0.0375	−0.0584
400	−0.0088	0.0000	−0.0164	0.0000	−0.0402	−0.0279	−0.0350	−0.0322	−0.0637
500	−0.0043		−0.0119		−0.0058		−0.0415	−0.0194	−0.0489
600	−0.0041	0.0000	−0.0076	0.0000	+0.0220	−0.0146	+0.0232	−0.0112	−0.0295
800	0.0000	0.0000	−0.0035	0.0000	+0 0373	+0.0034	+0.0564	+0.0174	+0.0236
1000	0.0000	0.0000	0.0000	0.0000	+0.0520	+0.0094	+0.0749	+0.0294	
Av..	0.0031	0.0000	0 0103	0.0031	0.0330	0 0193	0.0585	0.0230	0 0464
V_∞..	0.0007200		0.0008525		0.001250		0.001025		0.001250

SUMMARY

In this paper additional calculations are presented showing the P–V–T relations of single and composite gases over the widest temperature and

pressure ranges thus far investigated. The P–V–T relations are interpreted with the aid of a simple algebraic expression of one constant which increases with the increase in the molecular weight of the gas, but which approaches unity with increase in temperature for all the gases and their mixtures thus far studied. This phenomenon is illustrated arithmetically in table 1 and graphically in figure 3 of this article and in figure 5 of the previous article.

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KINETICS OF THE FORMATION OF SULFONIC ACIDS FROM DITHIO ACIDS. I

THE OXIDATION OF CYSTINE TO CYSTEIC ACID BY THALLIC SULFATE[1]

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The mechanism of the oxidation and reduction reactions of sulfur compounds of the type R—S—S—R and R—SH is of interest because of the peculiar chemical reactions of these substances, their widespread occurrence in biological materials, and their supposed participation in the oxidation and reduction systems of the living organism.

When R—SH and R—S—S—R compounds are treated with sufficiently powerful oxidizing agents, the end product, if the organic radical is not attacked, usually is the corresponding sulfonic acid, R—SO_3H. The direct oxidation pathway might be represented as follows:

$$2(\text{R—SH}) \xrightarrow{-2H} \text{R—S—S—R} \xrightarrow{+O+H_2O} 2(\text{R—SOH}) \xrightarrow{+O} (\text{R—SO}_2\text{H}) \xrightarrow{+O} \text{R—SO}_3\text{H}$$

The existence of the intermediates, R—SOH and R—SO_2H or their derivatives, for this series has not been demonstrated by stepwise oxidation of such sulfur compounds in aqueous solutions.

Recent investigations of the reactions of metallic salts with R—S—S—R demonstrate the formation of R—SO_3H and R—SH according to the following equation

$$3\text{R—S—S—R} + 3H_2O = 5\text{R—SH} + \text{R—SO}_3\text{H}$$

This reaction appears to be an intramolecular oxidation-reduction driven by the removal of R—SH in the following series of hypothetical equilibria:

$$\text{R—S—S—R} + H_2O \rightleftarrows \text{R—SH} + \text{R—SOH}$$
$$\text{R—SOH} + H_2O + \text{R—S—S—R} \rightleftarrows 2\text{R—SH} + \text{R—SO}_2\text{H}$$
$$\text{R—SO}_2\text{H} + H_2O + \text{R—S—S—R} \rightleftarrows 2\text{R—SH} + \text{R—SO}_3\text{H}$$

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The R—SH may be removed by precipitation as a silver salt by Ag^+ (6, 10), or as a mercuric salt by Hg^{++} (2, 9), through formation of an unionized complex by mercuric halide ions $BrHg^+$ (7), or through a combination oxidation and precipitation as a cuprous salt by Cu^{++} (8). If the R—SH formed in the above reaction with water is not removed but instead is reoxidized to R—S—S—R, there would be a continuous accumulation of R—SO_3H, which would ultimately appear as a complete conversion of R—S—S—R into R—SO_3H.

Since the possibility of isolating and identifying certain of the intermediates seems remote, an attempt has been made to obtain information concerning the mechanism of the reaction by kinetic measurements of the oxidation of R—S—S—R to R—SO_3H by various oxidizing agents.

The oxidation of cystine, $HOOC \cdot CHNH_2 \cdot CH_2S \cdot SCH_2 \cdot CHNH_2 \cdot COOH$, by thallic sulfate was selected, because with this oxidizing agent the reaction proceeds essentially quantitatively to cysteic acid, $HOOC \cdot CHNH_2 \cdot CH_2SO_3H$ and thallous sulfate. Thallic sulfate, further, forms with thallous sulfate a reversible oxidation-reduction system of known potential or oxidizing intensity, so that the results obtained may be useful for comparison with the data being obtained for other reversible oxidation-reduction systems.

EXPERIMENTAL

Preparation of reagents

Since chloride, bromide, and iodide were found to have unusual catalytic effects upon the reaction, special care was exercised in the selection of materials and preparation of solutions to insure that these substances would not be present in significant quantities.

Thallic oxide was suspended in 2.000 *N* sulfuric acid and dissolved by warming and concentrating to about 4 *N*. After proper dilution, the final solution was 0.005 gram-atomic in thallic sulfate and 1.000 *N* in sulfuric acid.

Cystine was prepared by the customary hydrochloric acid hydrolysis of hair and purified by several precipitations from sulfuric acid solution by sodium carbonate. The purity was checked by nitrogen determinations made by West and Brandon (11). The final solution was 0.01 *M* in cystine and 1.000 *N* in sulfuric acid.

Experimental procedures

The required amounts of sulfuric acid, water, and thallic sulfate were measured into a 250-cc. wide-mouth Pyrex flask which was immersed in a thermostat maintained within 0.1°C. At zero time the cystine solution was pipetted into the flask, which was shaken rapidly.

The reaction was stopped by suddenly adding 1 g. of potassium iodide in

25 cc. of water. The excess thallic salt was determined by adding freshly prepared starch as indicator, and immediately titrating with 0.01 *N* sodium thiosulfate, drop by drop, in diffuse or artificial light. The color change was from a greenish blue, through yellowish green, to the final bright yellow suspension of precipitated thallous iodide. Before again using the reaction flasks, they were thoroughly cleaned with chromic-sulfuric acid mixture. Ten such experiments with different time intervals determined the reaction rate constant for the particular conditions.

Determination of the products of the reaction

Several typical experiments were made with 60 cc. of 0.005 gram-atomic thallic sulfate solution reacting with 5 cc. of 0.01 *M* cystine solution at 30°C. The amount of thallic salt reduced (see table 1) approaches a maximum of 10 oxidation-reduction equivalents per mole of cystine, which suggests the equation

$$2HOOC\cdot CHNH_2\cdot CH_2S\cdot SCH_2\cdot CHNH_2\cdot COOH + 5Tl_2(SO_4)_3 + 12H_2O = 4HOOC\cdot CHNH_2\cdot CH_2SO_3H + 5Tl_2SO_4 + 10H_2SO_4$$

Experiments with the related dithiodihydracrylic acid, $HOOC\cdot CH_2\cdot CH_2S\cdot SCH_2\cdot COOH$, gave further indication that R—S—S—R type acids are oxidized almost entirely to $R—SO_3H$ acids. Mixtures of 0.07317 g. of this acid as the disodium salt and 20 cc. of 0.174 *N* thallic perchlorate in *N* perchloric acid were allowed to react for 40 hours at 37°C. The $Ba(\cdot OOC\cdot CH_2\cdot CH_2\cdot SO_3\cdot)$ formed was isolated and analyzed according to a modification of the procedure previously reported (6). The $R—SO_3H$ yield was 99 per cent of the theoretical and all except a trace of thallic salt was reduced (see table 2).

RESULTS OF KINETIC EXPERIMENTS

Mathematical considerations

The equation of the reaction indicates that 5 gram-atoms of thallic are reduced as 1 mole of cystine is oxidized. To permit the use of the less complex equations applying to pseudo first-order reactions, the cystine concentration was always made sufficiently high so that its initial concentration would change less than 10 per cent during the period of measurement. In calculating the reaction rate constants, only values between 20 and 80 per cent complete reaction were included and the arithmetical average of ten determinations, nearly equally spaced with respect to time, within this range, was considered sufficiently representative of the reaction rate under the particular conditions of the experiment. With but very few exceptions, the maximum variation of the constant in a particular series of ten values is less than 10 per cent. Table 3 gives the results of a typical series of determinations.

TABLE 1

Determination of the maximum number of reducing equivalents of cystine towards thallic sulfate

MINUTES AT 30°C.	EQUIVALENTS OF THALLIC SULFATE PER MOLE OF CYSTINE	MINUTES AT 25°C.	EQUIVALENTS OF THALLIC SULFATE PER MOLE OF CYSTINE
30	4.652	840	9.800
60	6.464	840	9.900
120	8.142	2400	9.980
180	8.720	2400	10.002
240	9.242		
300	9.406		
480	9.780		
840	9.876		
1240	9.994		
1470	10.012		

TABLE 2

Quantity of sulfonic acid produced from dithiodihydracrylic acid by thallic sulfate

Ba ($\cdot OOC \cdot CH_2\ CH_2 \cdot SO_3 \cdot$) ISOLATED	PER CENT Ba
grams	
0.1982	47.0
0.2010	47.0
0.1992	47.0
0.1979	47.2
0.1995	47.1
Av. = 0.1992	47.1
Theor. = 0.2015	47.4

TABLE 3

The results of a typical series of determinations

Temperature, 30°C.; thallic sulfate concentration 0.0005 gram-atomic; sulfuric acid concentration, 0.5 *N*; cystine concentration, 0.002 *M*

MINUTES	FRACTION OF THALLIC REDUCED	*k* (PSEUDO FIRST ORDER)
3	0.263	0.102
4	0.330	0.100
5	0.418	0.108
6	0.453	0.101
7	0.524	0.106
8.5	0.589	0.105
10	0.650	0.105
12	0.717	0.105
14	0.761	0.102
16	0.800	0.101
Average		0.104

From the pseudo first-order constant calculated from the disappearance of thallic salt, the second-order constant may be calculated by dividing by the concentration of cystine. The value so obtained represents the rate at which the thallic salt was being reduced, calculating on a gram-atomic thallic and a molar cystine basis; the rate of cystine oxidation is only one-fifth of this rate.

The results are summarized in tables 4 through 8. Each experiment numbered x is the same as some experiment listed in another table which has been inserted twice to preserve unity. Experiments lettered are inserted to show special effects of changing several variables.

TABLE 4

Effect of the concentration of the reactant, thallic sulfate, upon the rate of reaction at 30°C.

EXPERIMENT NO	INITIAL CONCENTRATIONS			K (PSEUDO FIRST ORDER)	K (SECOND ORDER)
	Cystine	$Tl_2(SO_4)_3$	H_2SO_4		
	gram-moles	*gram-atoms* Tl	*gram-equivalents*		
1	0.001	0 000125	1 0	0 0151	15.1
2	0 001	0.0001875	1 0	0 0177	17.7
3	0.001	0 00025	1 0	0 0197	19.7
4	0 001	0 000375	1 0	0 0220	22 0
5	0 001	0.0005	1.0	0.0234	23.4
6	0 001	0 001	1.0	0.0233	23.3
7	0 001	0.002	1.0	0 0227	22 7
A	0 001	0 00025	0.5	0.0478	47.8
Bx	0 001	0 0005	0.5	0 0547	54 7
C	0 001	0.001	0 5	0.0564	56.4

Thallic concentration effects

The values of K increase with an increase in thallic concentration until 0.0005 gram-atomic is reached; then nearly constant values are attained, showing that the reaction rate is probably proportional to the thallic concentration.

The oxidation-reduction potential values show similar changes (1), becoming less oxidizing as the thallic concentration is decreased below 0.0005 gram-atomic while keeping the thallic–thallous ratio the same. Whether the potential and rate changes are related remains for further work to decide.

Cystine concentration effects

As the concentration of cystine is increased there is a slight decrease in K (see table 5). At values above 0.002 molar, K becomes nearly constant,

so that the reaction rate may be considered proportional to the cystine concentration.

TABLE 5

Effect of the concentration of the reactant, cystine, upon the rate of reaction at 30°C.

EXPERIMENT NO.	INITIAL CONCENTRATIONS			K (PSEUDO FIRST ORDER)	K (SECOND ORDER)
	Cystine	$Tl_2(SO_4)_3$	H_2SO_4		
	gram-moles	*gram-atoms* Tl	*gram-equivalents*		
11	0.0005	0.0005	1.0	0.0123	24.6
12	0.00075	0.0005	1.0	0.0169	22.7
13x	0.001	0.0005	1.0	0.0234	23.4
14	0.002	0.0005	1.0	0.0420	21.0
15	0.003	0.0005	1.0	0.0600	20.0
16	0.004	0.0005	1.0	0.0791	19.8
17	0.005	0.0005	1.0	0.097	19.4
21x	0.001	0.001	1.0	0.0233	23.3
22	0.002	0.001	1.0	0.0422	21.1
23	0.003	0.001	1.0	0.0625	20.8
24	0.004	0.001	1.0	0.0807	20.2
25	0.005	0.001	1.0	0.103	20.6
D	0.0005	0.0005	0.5	0.0294	68.8
Ex	0.001	0.0005	0.5	0.0547	54.7
F	0.002	0.0005	0.5	0.104	52.0

TABLE 6

Effect of the concentration of the product, thallous sulfate, upon the rate of reaction at 30°C.

EXPERIMENT NO.	INITIAL CONCENTRATIONS				K (PSEUDO FRST ORDER)	K (SECOND ORDER)
	Cystine	$Tl_2(SO_4)_3$	Tl_2SO_4	H_2SO_4		
	gram-moles	*gram-atoms* Tl	*gram-atoms* Tl	*gram-equivalents*		
31	0.001	0.0005	0.0025	1.0	0.0237	23.7
31x	0.001	0.0005		1.0	0.0234	23.4
32	0.001	0.00025	0.0025	1.0	0.0204	20.4
32x	0.001	0.00025		1.0	0.0197	19.7
33	0.001	0.000375	0.001875	1.0	0.0233	23.3
33x	0.001	0.000375		1.0	0.0220	22.0
34	0.001	0.0005	0.005	0.5	0.0552	55.2
34x	0.001	0.0005		0.5	0.0547	54.7

Thallous sulfate concentration effects

The lack of significant change in the ten pseudo first-order constants obtained in a particular experiment and the close agreement between the values of K (see table 6) for experiments with and without initially added

TABLE 7

Effect of the concentration of sulfuric acid upon the rate of reaction at 30°C.

EXPERIMENT NO	INITIAL CONCENTRATIONS			K (PSEUDO FIRST ORDER)	K (SECOND ORDER)
	Cystine	$Tl_2(SO_4)_3$	H_2SO_4		
	gram-moles	*gram-atoms* Tl	*gram-equivalents*		
41	0.001	0.0005	0 25	0.143	143.0
42	0 001	0.0005	0 375	0.0918	91.8
44	0.001	0.0005	0.5	0 0547	54.7
44	0 001	0 0005	0.75	0.0335	33.5
45	0.001	0 0005	1 0	0 0238	23.8
46	0.001	0 0005	1 25	0 0163	16 3
47	0.001	0 0005	1.5	0.0135	13.5
48	0 001	0 0005	1 8	0 0113	11 3

TABLE 8

Effect of temperature on the rate of reaction at different acidities

EXPERIMENT NO	TEMPERATURE	INITIAL CONCENTRATION			K (PSEUDO FIRST ORDER)	K (SECOND ORDER)
		Cystine	$Tl_2(SO_4)_3$	H_2SO_4		
	degrees C	*gram-moles*	*gram-atoms* Tl	*gram-equivalents*		
1 T	15	0 001	0 0005	0.25	0.0171	17.1
2 T	15	0.001	0.0005	0.5	0 00720	7.20
3 T	20	0.001	0.0005	0.25	0.0319	31.9
4 T	20	0.001	0.0005	0.5	0 0137	13.7
5 T	20	0 001	0 0005	1 0	0 00587	5.87
6 T	25	0.001	0.0005	0 25	0.0709	70.9
7 T	25	0.001	0 0005	0 5	0 0287	28.7
8 T	25	0 001	0 0005	1 0	0 0117	11.7
9 Tx	30	0.001	0.0005	0.25	0.143	143.0
10 Tx	30	0.001	0.0005	0.5	0.0547	54.7
11 Tx	30	0.001	0.0005	1.0	0.0238	23.8
12 T	35	0.001	0.0005	0.5	0.100	100.0
13 T	35	0 001	0 0005	1 0	0 0404	40.4

thallous, indicate that thallous concentration and consequently also the oxidation-reduction potential of the thallic–thallous system have no apparent effect on the reaction rate.

Sulfuric acid concentration effect

The reaction rate decreases with an increase in sulfuric acid concentration (see table 7). No simple relation could be found between the rate and several of the usual methods of expressing acidities, and considering that cystine has two acidic and two basic ionizations in or near the region of acidity used, this is not surprising.

Temperature effects

The reaction rates at three acidities were determined (see table 8), and the graph of the reciprocal of the absolute temperature plotted against the logarithm of K results in three parallel lines whose slope is such that $Q = 24{,}200$ calories in the Arrhenius equation (3).

DISCUSSION AND SUMMARY

The kinetic experiments performed indicate that the rate-controlling step in the measured reaction between thallic sulfate and cystine in sulfuric acid solution is a second-order reaction.

The rate of reaction is approximately proportional to the cystine concentration and the thallic sulfate concentration and decreases with an increase in the sulfuric acid concentration. The equation for the complete reaction is

$$2HOOC\cdot CHNH_2\cdot CH_2S\cdot SCH_2\cdot CHNH_2\cdot COOH + 5Tl_2(SO_4)_3 + 12H_2O = 4HOOC\cdot CHNH_2\cdot CH_2SO_3H + 5Tl_2SO_4 + 10H_2SO_4$$

and indicates that 5 gram-atoms of thallic are reduced as 1 gram-mole of cystine is oxidized. At 30°C. in 1 N sulfuric acid with 0.0005 gram-atomic thallic sulfate and 0.001 M cystine, the value of the second-order constant for thallic reduction is $K_{Tl} = 23.3$ gram-atoms per minute per liter; for cystine oxidation under the same conditions $K_{Cys.} = 4.7$ moles per minute per liter.

Since several second-order reactions are possible in the series leading from R—S—S—R to R—SO_3H, the identification of a particular reaction is not possible with the data at hand. However, two reactions can be eliminated as being involved in the rate-controlling step with thallic salt as oxidant: the reaction of R—S—S—R with H_2O to give R—SH and R—SOH, since this would result in the reaction being independent of the concentration of the thallic salt; and the oxidation by thallic salt of R—SH formed by hydrolysis, since this oxidation would probably not be a simple bimolecular reaction. The approximate constancy of $K_{\text{pseudo first order}}$ in a particular series and the lack of an appreciable effect upon the rate of reaction upon the addition of thallous salt practically eliminates the possibility that the rate-controlling step involves a labile, reversible, electromotively

active oxidation-reduction system (4, 5) composed of intermediate oxidation stages of the sulfur compounds.

The energy of activation, Q, was found to be 24,200 calories at various acidities.

The oxidation of R—S—S—R to R—SO_3H by various oxidizing agents is being studied in the hope of solving the problem of the mechanism of this complex oxidation.

The authors are indebted to Dr. P. A. Shaffer for his many helpful suggestions and his constant interest in the work.

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KINETICS OF THE FORMATION OF SULFONIC ACIDS FROM DITHIO ACIDS. II

THE POSITIVE AND NEGATIVE CATALYTIC EFFECTS OF HALIDES UPON THE OXIDATION OF CYSTINE TO CYSTEIC ACID BY THALLIC SULFATE[1]

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During the oxidation of cystine (R—S—S—R—) to cysteic acid (R—SO_3H) by thallic sulfate (1), it was found that whereas high concentrations of iodide could be used to inhibit or stop the reaction, lower concentrations caused great acceleration of the rate of reaction. An investigation of this interesting and unusual effect of iodide and the effects of the other halides has been made to obtain additional information on the mechanism of the oxidation of R—S—S—R to R—SO_3H.

CATALYSIS AND INHIBITION BY IODIDE

The final result of the reaction between cystine and thallic sulfate can be represented (1) by the equation,

$$2HOOC\cdot CHNH_2\cdot CH_2S\cdot SCH_2\cdot CHNH_2\cdot COOH + 5Tl_2(SO_4)_3 + 12H_2O = 4HOOC\cdot CHNH_2\cdot CH_2SO_3H + 5Tl_2SO_4 + 10H_2SO_4$$

which apparently holds also for the iodide catalysis. A series of experiments was performed in which 60 cc. of 0.005 gram-atomic thallic sulfate in *N* sulfuric acid and 10 cc. of 0.001 *M* potassium iodide were allowed to react for 1 minute at 27°C. and then 5 cc. of 0.01 *M* cystine in 1 *N* sulfuric acid was added. The amount of thallic reduced was as follows:

Time (in minutes)	0.5	1	2	5	20	90
Reduction (in equivalents per mole of cystine)	8.036	9.900	9.896	9.880	9.984	9.960

The procedure used in the experiments which follow was identical with that used in the preceding paper. The halide solutions were made from

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samples selected for their high purity and absence of significant quantities of the other halides.

Effect of iodide concentration

When the potassium iodide, thallic sulfate, and sulfuric acid were mixed and allowed to interact for various periods of time, and then the cystine was added and allowed to react for a particular period of time, the amount of thallic reduced was found to decrease slightly with an increase in the first time period. This same result was obtained when the reaction took place under nitrogen. When cystine, potassium iodide, and sulfuric acid were mixed and allowed to stand for varying time periods and then thallic added, no difference in the amount of reduction was noted. The latter procedure was adopted, although the retarding effect cannot be eliminated completely even in this manner, since the iodide thallic reaction undoubtedly proceeds

TABLE 1

Calculation of a typical experiment

Reaction mixture: 0.0005 gram-atomic $Tl_2(SO_4)_3$, 0.001 *M* cystine, 1.0 *N* H_2SO_4, and 0.000,002 *M* KI. Temperature, 30°C.

TIME	FRACTION PRESENT AT BEGINNING OF THE MINUTE PERIOD	TOTAL FRACTION REDUCED	FRACTION OF UNCATALYZED REACTION IN PAST MINUTE	TOTAL UNCATALYZED REACTION	TOTAL KI-CATALYZED REACTION
minutes					
0	1.000				
1	0 799	0 201	0 022	0 022	0.179
2	0.612	0.388	0.018	0 040	0.348
3	0.442	0 558	0 013	0 053	0.505
4	0.286	0.714	0 010	0 063	0.651
5	0.100	0.900	0 006	0 069	0.831

simultaneously with the positive catalytic reaction; however, when the total reaction time is short, the error thus introduced is small.

The amount of reaction due to the catalytic effect was determined by correcting the experimental values for the normal uncatalyzed reaction going on at the same time (1). As an example, the corrections made on the reaction with 0.000,002 *M* potassium iodide and 0.0005 gram-atomic thallic sulfate are given.

The fraction of the total reaction which took place in 1 minute was calculated. Then the appropriate fraction of the normal reaction taking place in the preceding time was subtracted from each experimental value. (See table 1).

The values of $K_{catalytic}$ listed in table 2 are the arithmetic means of the values obtained for 1-minute intervals in the series. They represent the

number of oxidizing equivalents of thallic reduced (at the concentrations specified) per liter per minute per mole of iodide initially present.

The positive catalytic effect of iodide first becomes noticeable at 0.000,-000,1 *M* potassium iodide and increases until a maximum is reached at about 0.000,05 *M*, after which the effect diminishes, and at 0.01 *M* and higher the rate becomes even less than when iodide is absent (see table 2).

Effect of thallic sulfate concentration

The catalysis depends also upon the ratio of the initial iodide to initial thallic concentrations (see table 2). For the three experiments where $(I^-)/(Tl^{+++}) = 0.002$, the fractions of thallic reduced in a given time through catalysis are essentially the same. Similar relationships hold also for certain other ratios.

When the ratio is changed by varying the initial iodide concentration, the rate of catalytic reduction increases as the ratio is increased. For the higher accelerating concentrations, the effect of the initial thallic concentration becomes less pronounced and the rate is only slightly increased as the ratio is increased and appears to be proportional to iodide alone.

During a particular series of experiments, the ratio of $(I^-)/(Tl^{+++})$ increases with an increase in time, because of the reduction of the thallic to thallous. The catalytic rate remains almost constant. These results might be explained on the assumption that the thallic reacts very rapidly with iodide to form a quantity of unreactive, slowly dissociating complexes, thereby preventing some of the iodide from taking part in the catalytic reaction.

Effect of cystine or thallous sulfate concentration

Cystine or thallous sulfate concentration changes do not alter the catalytic reduction rate.

Effect of sulfuric acid concentration

Increases in the sulfuric acid concentration cause the catalytic reaction rate to decrease. For a mixture of 0.0005 gram-atomic thallic, 0.001 *M* cystine, and 0.000,001 *M* iodide at 30°C., the difference in rate at 0.5 *N* and 1.5 *N* acid is about 40 per cent.

Effect of temperature

The effect of temperature on iodide catalysis was determined by a group of experiments at 0.0005 gram-atomic thallic, 0.001 *M* cystine, in *N* acid with various initial iodide concentrations and temperatures (see table 3). The temperature coefficient, *Q*, is 21,700 calories for that part of the reaction apparently proceeding through iodide catalysis. For the uncatalyzed reaction $Q = 24,200$ calories (1).

TABLE 2

Effect of iodide and thallic concentrations

KI	$Tl_2(SO_4)_3$	$\frac{(I)}{(Tl^{III})}$	K (CATALYTIC) AVERAGE	TIME IN MINUTES 0.5	1 0	1 5	2	3	4	5	6	7	8	9	10	15	20	25	30	40
moles per liter	*gram-atoms per liter*														Fraction $Tl_2(SO_4)_3$ reduced					
0.0	0.000,125	0.000														0.214	0.268	0.307	0.353	
	0.000,25															0.245	0.318	0.370	0.422	0.558
	0.000,5														0 197	0.280	0.341	0.412	0.471	0.576
	0.001														0 210	0.300	0 374	0.425	0.499	0.610
				Fraction $Tl_2(SO_4)_3$ reduced (total)																
				Fraction $Tl_2(SO_4)_3$ reduced through iodide (calculated)																
0.000,000,1	0.000,5	0.0002													0.228	0.327	0.405	0.481	0.539	0.651
															0.034	*0.053*	*0.062*	*0.077*	*0.082*	*0.106*
0.000,000,5	0.000,125	0.004	(103,500)		0.239		0.451	0.645												
					0.224		*0.425*	*0 611*												
	0.000,25	0.002	78,000				0.203	0.291	0.372	0.480	0.552	0.649	0.746	0.816	0.903					
							0.167	*0.240*	*0.308*	*0.404*	*0.466*	*0.554*	*0.644*	*0.709*	*0.792*					
	0.000,5	0.001	62,000						0.228	0.274	0.322	0.376	0.421	0.469	0.502	0.708	0.908			
									0.142	*0.171*	*0.230*	*0.242*	*0.273*	*0.308*	*0.329*	*0.482*	*0.650*			
0.000,001	0.000,25	0.004	85,000		0.186		0.383	0.553	0.743											
					0.167		*0.349*	*0.507*	*0.689*											
	0.000,5	0.002	79,000				0.221	0.316	0.392	0.492	0.575	0.670	0.757	0.842	0.930					
							0.177	*0.255*	*0.316*	*0.403*	*0.475*	*0.561*	*0.641*	*0.721*	*0.806*					

	0.001	0.001	64,000						0.242	0 283	0.328	0.379	0.430	0.469	0.518	0.715	0.901		
									0 156	*0.180*	*0.209*	*0.245*	*0.282*	*0.308*	*0 345*	*0.490*	*0.646*		
0.000,002	0.000,5	0.004	83,000		0.201		0.388	0.558	0.714	0.900									
					0.179		*0 348*	*0 505*	*0.651*	*0.831*									
	0.001	0.002	77,000				0.233	0.327	0.412	0 502	0.589	0.665	0.750	0.837					
							0 189	*0 266*	*0 336*	*0 413*	*0.489*	*0.556*	*0 634*	*0.716*					
0.000,005	0.000,5	0.01	92,000	0 260	0.489	0.730	0 950												
				0.249	*0.470*	*0 705*	*0.922*												
0.000,01	0.000,5	0.02	(97,800)	0.500															
				0.489															
0.000,01	0.001	0 01	87,800	0.279	0.481	0.694	0.906												
				0.268	*0.462*	*0.669*	*0.878*												
0.000,05	0.000,5	0.1		(1.00)															
0.000,1	0.000,5	0.2		(0 91)															
0.000,5	0.000,5	1.0		(0.64)															
0.001	0.000,5	2.0		(0.53)															
0.01	0.000,5	20.0		0.003	0.000														

EFFECTS OF CHLORIDE, BROMIDE, AND FLUORIDE

The results obtained with chloride or bromide under conditions similar to those used with iodide may be briefly summarized. Essentially complete and immediate inhibition occurs when the halide–thallic ratio is 2 or greater. There is no appreciable accelerating effect. Fluoride shows neither a catalytic nor an inhibitory effect.

Rather unexpected is an enhanced acceleration induced by bromide, and to a lesser extent by chloride in the iodide-catalyzed reaction.

TABLE 3

Effect of temperature on iodide catalysis

IODIDE CONCENTRATION	TEMPERATURE t	TEMPERATURE T	$1/T$	AVERAGE K*	$\log_{10}$ AVERAGE K*
moles	*degrees C.*	*degrees A.*			
0.000,000,5	35	308	0.3247	0.055	−1.2596
0.000,001	35	308	0.3247	0.138	−0.8601
0.000,000,5	30	303	0.3300	0.034	−1.4685
0.000,001	30	303	0.3300	0.081	−1.0915
0.000,002	30	303	0.3300	0.170	−0.7696
0.000,005	30	303	0.3300	0.475	−0.3233
0.000,000,5	25	298	0.3356	0.017	−1.7696
0.000,001	25	298	0.3356	0.044	−1.3565
0.000,002	25	298	0.3356	0.099	−1.0044
0.000,005	25	298	0.3356	0.265	−0.5768
0.000,001	20	293	0.3413	0.022	−1.6576
0.000,002	20	293	0.3413	0.053	−1.2757
0.000,005	20	293	0.3413	0.141	−0.8508
0.000,001	15	288	0.3472	0.012	−1.9208
0.000,002	15	288	0.3472	0 026	−1.5850
0.000,005	15	288	0.3472	0.076	−1.1192

* Equivalents of thallic reduced per liter per minute in a solution 0.0005 gram-atomic in thallic, 0.001 M in cystine, and 1.0 N in sulfuric acid.

DISCUSSION

The uncatalyzed reduction of thallic sulfate by cystine is a second-order reaction (1) and may be represented by $K = 23.3$ gram-atoms reduced (in a gram-atomic thallic solution molar in cystine and normal in sulfuric acid) per liter per minute. For the iodide-catalyzed reaction, K becomes somewhat greater as the initial iodide is increased and becomes less as the initial thallic is increased within certain ranges.

The value of $K_{catalytic}$ obtained by calculation as described on the basis

of initial iodide approximates 80,000 to 100,000 oxidation-equivalents of thallic reduced per liter per minute per mole of initially added iodide for certain specific conditions.

The iodide catalysis appears to be a zero-order reaction over a wide range of concentrations, when proper allowance is made for the effect of thallic concentration on the initial iodide.

The inhibiting effects of chloride, bromide, and iodide are probably due to the formation of complex ions or groups with thallic. The conclusion is supported by the effects introduced by thallic changes and also by the lack of effect of fluoride, which has little tendency to form complexes with thallic.

The accelerating effect of the halides may be due to the liberation of a highly reactive form or compound of the halogen which may react more rapidly with cystine. A comparison of the oxidation-reduction potential of the thallic–thallous system to those of the halogen–halide systems reveals that thallic could liberate the halogens from halides. Bromine alone or in the presence of large amounts of bromide oxidizes cystine to cysteic acid at an immeasurably fast rate. Shinohara (2) has demonstrated that iodine also oxidizes cystine to cysteic acid, but at a relatively slow rate. This result makes it appear unlikely that the positive iodide catalysis proceeds through the formation of some iodide derivative ordinarily present in significant quantity in an acidified potassium iodide solution of iodine.

The study of these unusual catalyses is being continued with various R—S—S—R compounds and oxidizing agents.

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STUDIES ON OVERVOLTAGE. VII

Electrode Discharge Phenomena Studied by Means of an Electromagnetic Interrupter together with an Oscillograph[1]

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In previous articles (1) the authors have studied polarization phenomena by means of a commutator in connection with a potentiometer, also by means of a commutator in connection with an oscillograph (2).[2] Comparisons were made of the direct and commutator methods for measuring such phenomena. The results of all the earlier work indicate that both methods give identical values for electrode potentials when measurements are properly made. This is contrary to the findings of most other investigators in this field. It is generally stated that the commutator method gives lower values than the direct. The difference between the two is attributed to a part of the voltage measured by the direct method being used up in driving the current through some kind of a resistance other than electrolytic resistance at the surface of the electrode. This resistance is commonly referred to as "transfer resistance" or "surface resistance." The existence of such a resistance has been postulated for about one hundred years. If a surface resistance exists, then, of course, a part of the applied potential, which is the thing measured by the direct method, is used up as an *IR* drop at the electrode–solution interface, and, naturally, the electrodes themselves are not charged to so high a potential. The back potential, which is measured by the commutator method, must be less, therefore, than the value which the direct method gives by an amount equal to the *IR* drop through the film on the electrode. It is assumed, of course, that account is taken of the ordinary *IR* drop through the solution.

One of the most active supporters of the transfer resistance idea is E. Newbery. He has made about fifty thousand observations with the rotat-

[1] The oscillograph used was purchased with a grant from the Faculty Research Fund of the University of Michigan, which thus made this work possible.

[2] Since the publication of this article, our attention has been called to two articles by S. K. Waldorf in which he made use of an amplifier-oscillograph arrangement similar to ours in his study of dielectrics (Physics **3**, 1 (1932); J. Franklin Inst. **213**, 605 (1932)).

ing commutator and about two thousand with the cathode ray oscillograph during a period of about twenty years.

It was shown in earlier papers by the authors that most of the measurements made by a rotating commutator are averages and therefore practically valueless so far as furnishing information upon the question of transfer resistance is concerned.

Those who defend the transfer resistance idea base their support largely upon an instantaneous drop in electrode potential, almost universally observed, immediately after the polarizing circuit is opened. As Newbery states in a recent article (3), "We will first utilize these curves for a discussion of the nature and properties of the very controversial 'transfer resistance.' The most striking feature of each of these curves (he refers here to electrode discharge curves obtained with a cathode ray oscillograph) is the clear gap which appears between the upper and lower sections. The existence of this gap proves conclusively that there is an instantaneous fall of potential at the electrode the moment the exciting current is interrupted. . . . . This resistance—transfer resistance—may be measured by observing the vertical height of the gap in the curves, calculating the corresponding change of E.M.F., and from this, calculating the resistance, the total current flowing being known. When this is done, it is found that although the gaps in the curves are wider at the higher current densities, the actual transfer resistances are lower. In fact, transfer resistance increases rapidly as the current density is lowered, and at very low current densities it is frequently above 100 ohms per sq. cm."

In an earlier article (2) the authors have presented results obtained with a rotating commutator in connection with a moving coil oscillograph that give no indication of an *IR* drop, except that due to the *IR* drop through the solution, when the charging circuit is suddenly opened.

The true nature of the drop in potential which takes place immediately after the polarizing circuit is opened could be determined much better if the curve representing such a drop could be superimposed upon another curve known to be due to an *IR* drop only; or on one known to be due to both an *IR* drop and the falling off of a true electrode potential. In the work to be described such an arrangement was used.

The desired result was accomplished by the substitution of an electromagnetic interrupter in place of the commutator. The circuits involved are represented in figure 1. The portion of the figure within the circle and labelled "Drum" represents the face of the rotating film drum. Supported in front of the drum are three pairs of bronze brushes, Br_1, Br_2, and Br_3. The pair of brushes Br_1 is short-circuited once during each revolution of the drum through the contact P_a. In a similar manner the pair Br_2 is short-circuited through P_b. The contacts P_a and P_b are permanently attached to the face of the drum, but contacts P_{c1}, P_{c2}, etc., are removable

and only one is used at a time. The portion of the drum included in the angle φ is not covered by the film. When the Br_1 brushes are short-circuited the electromagnet A closes the circuit through the lamp L of the oscillograph. Just following this the brushes Br_3 are short-circuited through the contact P_c in some one of the positions 1, 2, 3, etc. This closes the circuit through the electromagnet C, which opens the polarizing circuit I_p. In this manner the start of the discharge interval can be located at any one of several points throughout the length of the film. After the entire length of the film has been exposed the lamp is turned off by means of the

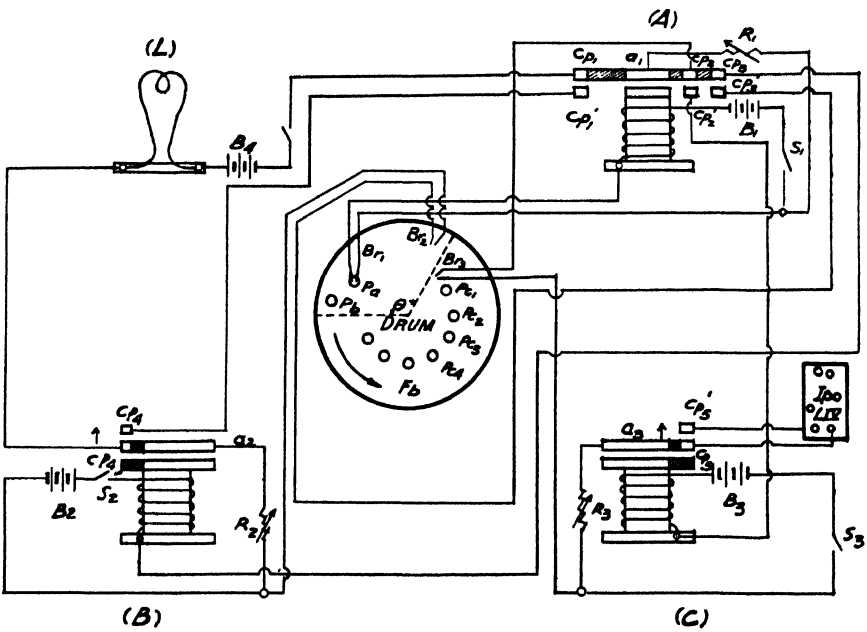

FIG. 1. CIRCUITS FOR ELECTROMAGNETIC INTERRUPTER

brushes Br_2 as they make contact at P_b, and thus the circuit through electromagnet B is closed.

As described in the previous article (2), the potential to be studied may first be measured with a potentiometer, which gives the value by the direct method; it is then applied to the grid circuit of the amplifier, and the voltage V_1 adjusted until the plate current as indicated by the ammeter is at some value near the upper part of the linear portion of the amplification curve. The plate current is then reduced to any desired value by the balancing potential V_2, so as to bring the line on any desired part of the width of the film. Although potentials of different magnitudes are applied to the grid circuit of the amplifier, it is possible by means of the

variable voltages V_1 and V_2 to cause the same current to pass through the oscillograph. Under such conditions the lines on the film which correspond to the various potentials are superimposed up to the point where the polarizing current is interrupted, and, if the contact P_c is in the same position on the drum face, each potential will be interrupted at the same point. The relative natures of the various discharging potentials may thus be directly determined.

In order to make a comparison between an IR drop and depolarization, pictures were taken of three types of potentials: (1) single electrode potential against its own reference electrode, which is either a pure potential or a pure potential plus a potential over transfer resistance; (2) single electrode potential against the opposite reference electrode, which is a pure potential plus the IR drop through the solution and plus an IR drop due to

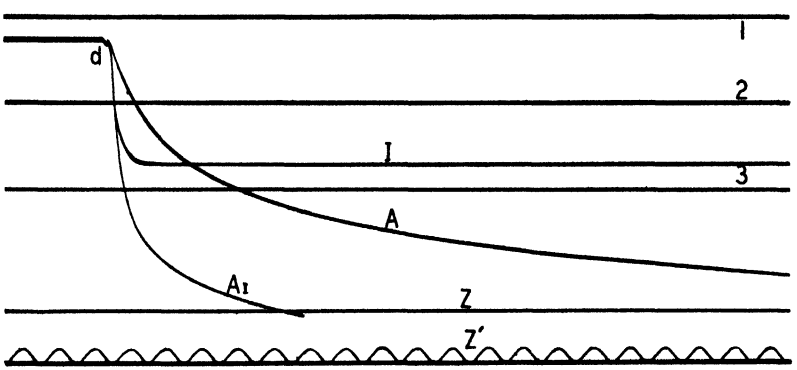

FIG. 2. DISCHARGE CURVES OF VARIOUS TYPES

A = potential of anode against anode standard; A_I = potential of anode against cathode standard; I = potential of anode standard against cathode standard.

transfer resistance, if any exists; (3) the potential between the reference electrodes, which is due only to the IR drop through the solution and any transfer resistances at the electrode surfaces. The same electrolysis system was used as described in a previous paper; the electrodes were platinized platinum and the solution 2 N sulfuric acid.

In figure 2 are three curves: A shows the drop in potential of the anode as measured against the anode standard; A_I shows the drop in potential of the anode as measured against the cathode standard, and includes, therefore, the IR drop through the solution; and I shows the IR drop through the solution only. The point d is the common breaking point for all the curves. The line to the left of d is heavy because it is common to all three curves.

It is universally accepted that the potential over a pure resistance should

drop instantaneously. Curve I, which pictures such a drop, is not vertical as it should be to show an instantaneous drop; this results from a slight lag in the vibrating element of the oscillograph. There can be no doubt, however, that A does not show any drop due to a resistance, which means there could have been no drop due to transfer resistance at the surface of the electrode included in the original potential measured by the direct method. It is clearly evident, on the other hand, that A_I does contain a drop due to resistance. The original potential of A_I contained all of the IR drop shown by I, and from the breaking point, d, the two curves are identical for some distance, and evidently would have remained identical down to the horizontal portion of I had it not been for a slowing-up of the vibrating element as it approached the end of its return swing for curve I. Another way to show that A_I contains the same IR drop as I, and no more or no less, is to measure the vertical distance between A and A_I which is

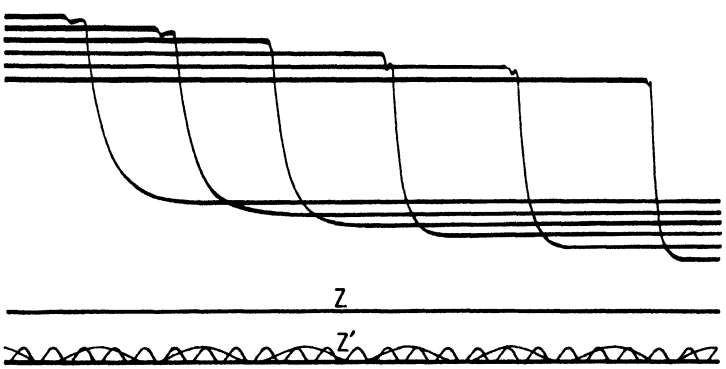

FIG. 3. CURVES TO SHOW THE TIME LAG IN THE VIBRATING ELEMENT OF THE OSCILLOGRAPH

found at all places to be equal to the total drop in I. Such a test was applied to several sets of curves and always held. To show the magnitude of the voltage changes, three constant voltage lines, 1, 2, and 3, were drawn across the film. The distance between 1 and 2 or between 2 and 3 is 40 millivolts. By means of the timing wave, which is for a 120-cycle current, the rate of fall of anode potential may be determined easily.

To learn something more definite about the lag of the vibrating element, a series of discharge curves, over a pure resistance, were taken with the same potential applied to the grid but with different balancing potentials so as to bring the curves at different positions on the width of the film. These curves are shown in figure 3. The contact point, P_c, was inserted in different positions so as to cause the break to appear at successive positions longitudinally on the film. The first curve was taken at the highest speed and the last at the lowest; the speeds are represented by the 120-cycle tim-

ing waves at the bottom. These curves show that what is really an instantaneous drop is not recorded on the film by a vertical line.

In figure 4 is shown a series of curves obtained with the same film speed, but for different resistances. These all represent potential drops due to pure resistances only, and show similar characteristics. The rate of drop is the same at the start, but slows up distinctly, and in about the same manner, as the element approaches its zero position. From the curves in figures 3 and 4 it would be possible to calculate the lag under a given set of conditions and apply it as a correction. It is evident from these oscillograms that when a curve produced by this oscillograph is analyzed to determine whether it contains a potential due to an IR drop, this lag of the vibrating element and variation of the lag with speed of film and displacement of element must be taken into account. The best way to do this is

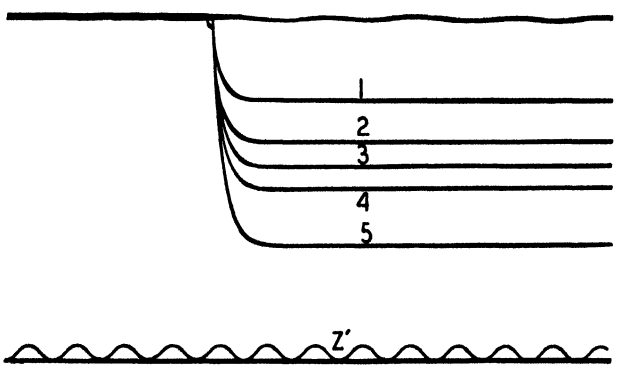

FIG. 4. POTENTIAL DROPS OVER A SERIES OF PURE RESISTANCES

For curve 1, R = 10 ohms; for 2, R = 15 ohms; for 3, R = 18 ohms; for 4, R = 20 ohms; and for 5, R = 30 ohms.

to superimpose the curves to be studied upon a curve representing a pure IR drop.

For very small currents it is not possible to distinguish between curves resulting from electrode depolarization and those caused by IR drop. This is evident from the curves in figure 5. These curves were taken for potentials above the decomposition point, but the current density was only 0.00053 amp.

The curves for slightly higher potentials are shown in figure 6. When the depolarization and IR drop curves are superimposed, it is just possible to distinguish between them in the case of the highest potential at the top of the film. The drop for I_1 is slightly more rapid at the start than K_1 and soon reaches a constant value, while K_1 continues to drop throughout the whole discharge interval.

A comparison of various types of discharge potentials at both anode and cathode is possible from the curves in figure 7. The current density during the photographing of all the curves in this figure was 0.0094 amp. The K

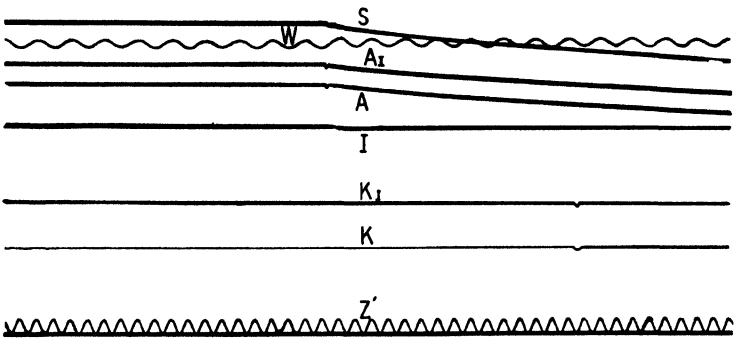

FIG. 5. DISCHARGE CURVES AT CURRENT DENSITY OF 0.00053 AMP.

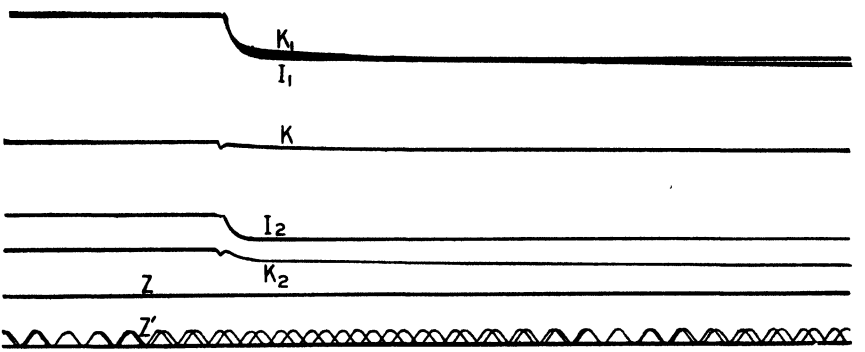

FIG. 6. DISCHARGE CURVES AT CURRENT DENSITIES OF 0.0020 AND 0.0026 AMP.

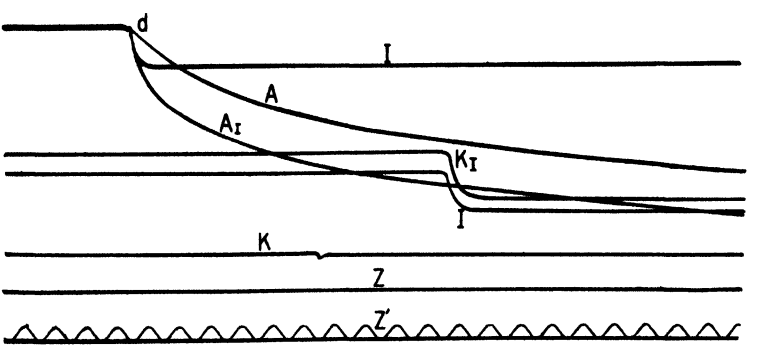

FIG. 7. A COMPLETE SET OF ANODE AND CATHODE DISCHARGE CURVES FOR AN APPLIED POTENTIAL, 2.040 V, ONLY SLIGHTLY ABOVE THE DECOMPOSITION POINT

curve shows there was practically no overvoltage at the cathode. The K_I and the I curves are practically identical as they should be, since K shows no overvoltage; but taken separately one would hesitate to say whether K_I represents electrode depolarization or an IR drop. The situation at the anode is clear-cut. There is no doubt that A contains no IR drop. A_I is definitely made up of the sum of the IR drop in I and the electrode depolarization in A. The curves A and A_I are parallel and the distance between them is the IR drop in I.

The curves in figure 8 are for a current density of 0.017 amp., about twice that in figure 7. Here again there can be no question about being able to distinguish between depolarization and an IR drop, especially if the curves are superimposed. There is no indication of an IR drop due to surface resistance of any kind at the anode. The S curve contains the depolariza-

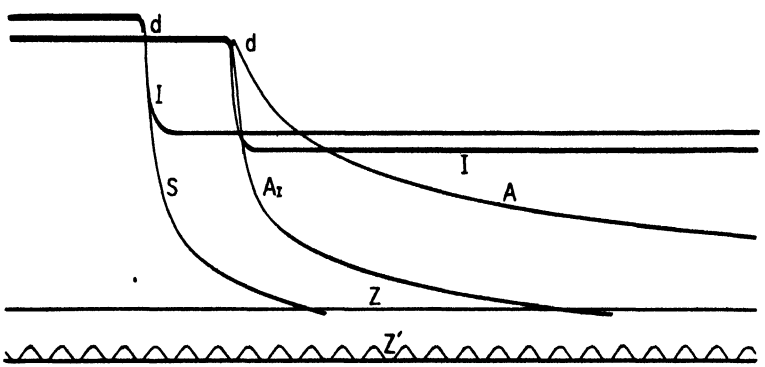

FIG. 8. DISCHARGE CURVES FOR A CURRENT DENSITY OF 0.017 AMP.

tion at both the cathode and anode and also the IR drop through the solution.

SUMMARY

1. An electromagnetic interrupter is described which makes it possible to open the charging circuit at any desired time interval after charging is started.

2. With this interrupter and accompanying alterations in the oscillograph it is possible to superimpose curves representing various types of potentials as determined by the direct method, and to interrupt the charging circuit at the same point on the film for each.

3. Owing to the lag in the vibrating element, the drop in potential over a pure resistance does not appear vertical.

4. Because of the great lag when the vibrating element has returned nearly to its zero point, it is not possible to distinguish between depolarization and an IR drop when the polarization is less than about 5 millivolts.

5. No curves that represent the potential between an electrode and its own reference electrode, i.e., that contain no known *IR* drop, show any indication of an *IR* drop due to surface resistance.

6. This work substantiates the conclusion arrived at in several earlier papers from this laboratory, that there is no transfer or surface resistance at platinized platinum electrodes in 2 *N* sulfuric acid.

The junior author wishes to acknowledge his indebtedness to the China Foundation for the Promotion of Education and Culture, for the granting to him of a fellowship which made it possible for him to continue his research work at the University of Michigan.

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(2) Ferguson and Chen: J. Phys. Chem. **36**, 2437 (1932).
(3) Newbery: Trans. Am. Electrochem. Soc. **58**, 187 (1930).

NEW BOOKS

Die Alkalichloridelektrolyse in Diaphragmazellen. By G. ANGEL. 19 x 13 cm.; 126 pp. Berlin: Verlag Chemie, G. m. b. H., 1933. Price: 12 M.

In this monograph the author has reëxamined the whole basis of the theory of the electrolysis of alkali chloride solutions in diaphragm cells. It is shown that when a true steady state has been established the current efficiency can be expressed as a function of the alkali concentration in the catholyte; the exactness of the relations deduced has been tested by numerous experiments with sodium chloride solutions in cells of the horizontal diaphragm type. Physical properties of the electrolyte have been measured under various conditions, and the density, viscosity, and conductivity of both anolyte and catholyte at various temperatures are related to the alkali concentration of the catholyte. Comparison of the theoretical relations for potassium and sodium chlorides indicates that, starting with solutions saturated at room temperature, the current efficiency in the steady state should be lower in the former than in the latter case. This conclusion, which is at variance with previously accepted statements, is shown to be borne out by experimental results.

The theoretical discussions and experimental results constitute an important contribution to the study of this complex subject and should prove of considerable value in the further development of technical cells and in the control of their operation. The main conclusions are summarized clearly at the end of each section of the book, and the experimental data are set out in numerous tables and graphs.

H. J. T. ELLINGHAM.

Die moderne Atomtheorie. Die bei der Entgegennahme des Nobelpreises 1933 in Stockholm gehaltenen Vorträge von W. Heisenberg, E. Schrödinger, and P. A. M. Dirac. 22 x 15 cm.; 45 pp. Leipzig: Verlag S. Hirzel, 1934. Price: 2.50 RM.

This collection of three Nobel lectures on related subjects deals, in succession, with the uncertainty principle, with the fundamental conceptions of wave mechanics, and with the theory of electrons and positrons. The subjects are dealt with in a broad and general way, yet in sufficient detail in each case to bring out the essential features. The advantage which every reader obtains from such a book depends on the mental background which he brings to it, but all physical chemists who are acquainted with the general notions of generalized coördinates, the quantum theory, and experimental physics will find these profound yet clearly written expositions of considerable interest, and will gain from them a picture of the broad features of certain aspects of modern atomic theory.

J. R. PARTINGTON.

Pflanzenthermodynamik. By KURT STERN. 22 x 15.5 cm.; xi + 412 pp. Berlin: Julius Springer, 1933. Price: unbound, 32 RM; bound, 33.20 RM.

This book is divided into two parts. The first is an exposition of the principles of thermodynamics; the second a description of their application to processes occurring in plants. In the former the author's stated object is to concentrate on those parts of the subject with a direct application to plants to the exclusion of those with little or no bearing on botany, but it is difficult to see in what respect this object has been achieved. The method of treatment, in fact, appears to be essentially a con-

densed version of that of Schottky, Ulich, and Wagner, but brevity has been gained only at the expense of lucidity and accuracy. The best feature of the treatment is the discussion of the most general physical principles, such as the first and second laws of thermodynamics, chemical equilibrium, and osmotic equilibrium. There is also a good, if out of place, review of photochemistry, which is not thermodynamics at all. The treatment of other topics is less fortunate. For instance, whereas emphasis is rightly laid on the distinction between total work and useful work (Nutzarbeit), the difference is not clearly defined. Again the well-known formula obtained for the efficiency of a Carnot cycle is applied to cycles of other types, for which its validity has not been demonstrated. This error occurs in almost all elementary textbooks, but the present book is not at all elementary. In fact the reviewer found it heavier reading than almost any of the most advanced treatises on thermodynamics.

The applications described in the second part of the book are of great interest. It is explained that, owing to the great experimental difficulty of obtaining accurate thermodynamic data with plant materials, only a low order of accuracy is possible. This being the case, surely a briefer and easier treatment would have been adequate as well as more attractive.

To sum up, the book should interest the reader whose chief concern is thermodynamics, by showing the importance of the subject for botany. It is, on the other hand, less likely to attract the botanist to a study of thermodynamics than to frighten him away from it.

E. A. GUGGENHEIM.

The Science of Radiology. Edited by Otto Glaser. 450 pp. Baltimore: Charles C. Thomas, 1933. Price: $4.50.

This collection of twenty-five papers on the various phases of the science of radiology is published under the auspices of the American Congress of Radiology and the editorship of Dr. Otto Glaser, who also contributes the first two papers on the history of the discovery of Roentgen rays and on the discovery of radium. The succeeding ten chapters are devoted to x-rays, including one by D. L. Webster on Roentgen-ray physics, one by W. D. Coolidge and E. E. Charlton on Roentgen-ray tubes, and one on therapy by U. V. Portmann. Several chapters deal with radium therapy and technique. Miscellaneous chapters treat Roentgen-ray protection, teaching of radiology, and industrial radiology. Leaving therapy entirely, the last two chapters comprise one by A. H. Compton on cosmic rays and one by William Seifriz on the mitogenic rays which he calls "Gurwitsch" rays. The author is not convincing in his defense of the reality of this much questioned type of radiation. Quantized energy relations are wholly neglected, though evidently important in attempting to decide whether light of ultra-violet wave length may be invoked as a cause of the observed phenomena.

The entire collection is highly creditable to the contributors and to the editor and will be indispensable to all who are interested in radiotherapy.

S. C. LIND.

Electrokinetic Phenomena and their Application to Biology and Medicine. By HAROLD A. ABRAMSON. American Chemical Society Monograph. 15.5 x 23.5 cm.; 331 pp.; 106 figs. New York: The Chemical Catalog Company, Inc., 1934. Price: $7.50.

This book will fill a great need in the field of physical chemistry and of its allies, biochemistry and biophysics. The reviewer has, for a number of years, been working in the field of electrokinetics and has acutely felt the need for a monographic treatment of the literature, which, until this volume appeared, has been scattered

through a great variety of texts and journals, many of which are almost inaccessible to the average worker.

Electrokinetics deals with the electrical behavior of the phase boundary at interfaces. The solid–liquid and liquid–liquid interfaces have been most widely studied, although unquestionably solid–gas and liquid–gas interfaces show similar phenomena. At these interfaces, electrokinetics is concerned with the so-called Helmholtz double layer, and should not be confused with the Nernst, or thermodynamic, or membrane potential.

The book opens with an excellent "Historical" chapter which adequately covers the literature from Reuss (1808) to Helmholtz (1879). This is followed by "Early theory and related experiments," where the contributions of Helmholtz, Quincke, Wiedemann, Lamb, von Smoluchowski, Perrin, Pellat and others, in building up the theory of a rigid double layer are considered. These chapters are followed by others on "Early confirmation of theory" and an excellent discussion of "Methods." A discussion of "Recent theory and related experiments," in which the reviewer was delighted to find a thorough treatment of the diffuse layer theory of Gouy and Debye and Hückel, closes the theoretical section.

Later chapters deal with "Proteins and some related compounds," "General effect of salts on inert surfaces," "Inorganic surfaces," "Organic surfaces," "Gases," "Blood cells, spermatozoa, tissues, etc.," and "Bacteria, antibodies, viruses, and related systems." An appendix follows, which includes a key to the mathematical symbols used in the formulas, a table of the numerical value of the various constants and factors, and a list of patents covering various phases of electrokinetic behavior. Author and subject indices close the volume.

Throughout the book the mathematical treatment is excellent. The author, while himself actively doing research in this field, presents impartially his own viewpoint and the viewpoints of others. One sometimes even wishes he were not such an impartial critic.

As one glances through the literature references one is impressed with the fact that the vast majority date since 1920. Industry, biology, and medicine have all profited by the use of electrokinetic technics. They will profit still more as workers in this field are multiplied, and this book will be a great assistance to that end. It is highly recommended to all who are interested in the solution of the problems of interfaces. It should be in all chemical, physical, and biophysical libraries. The price will be the only deterrent to its purchase by many individuals.

ROSS AIKEN GORTNER.

Physico-chemical Practical Exercises. By W. N. RAE AND JOSEPH REILLY. 19 x 13 cm.; xiv + 276 pp. London: Methuen and Co., 1934. Price: 7s. 6d.

The authors of the well-known book, "Physico-chemical Methods," now in its second edition, which is so useful to the advanced worker for reference, have here given us a much smaller volume, intended for students working for an honors degree in chemistry.

The book begins with a mathematical consideration of error, nomography, and calibration of apparatus. Important as this is, it would have been better, in the reviewer's opinion, to have placed this section at the end of the book. The student beginning work on physical chemistry is too apt to concentrate on the elimination of small errors and unknowingly introduce larger ones.

The experiments described, seventy-three in all, are many of them usual in such textbooks; there are, however, interesting additions, e.g., in surface tension, Jaeger's method, viscosity by the falling sphere, Rast and Menzies' methods in determination of molecular weight, and the use of the glass electrode and valve electrometer. On

the other hand, exercises not usually found in an elementary textbook are described: e.g., measurement of gas viscosity, vapor pressures, heat conductivity of gases, and the Nernst calorimeter.

Theory is introduced where necessary. There are seventy-four diagrams in the text, some of which might be improved, e.g., the Pulfrich refractometer, capillary electrometer etc.

The student who has the time in his degree course to work through all these experiments will have laid an excellent foundation for a study of physical chemistry and the book, at its reasonable price, can be strongly recommended.

W. H. PATTERSON.

Kristallchemie. By O. HASSEL. (Band 23 of Wissenschaftliche Forschungsberichte, Naturwissenschaftliche Reihe. 22 x 15 cm.; vii + 114 pp. Dresden and Leipzic: Steinkopff, 1934. Price: unbound, 9 RM; bound, 10 RM.

Until a year or so ago many of the existing treatises on x-rays and their applications to crystal physics and chemistry were rather out of date, and some of the latest views were only to be found in isolated papers. New editions of well-known works have now appeared, and in addition we have before us a small book by Dr. Hassel dealing with what is generally referred to in English as chemical crystallography. Dr. Hassel's own researches on coördination compounds are his passport to this field, and in *Kristallchemie* he has given a lucid account of the laws that may be deduced from crystal structure determinations by means of x-rays.

W. L. Bragg was the first to deduce approximate atomic radii from crystal-structure determinations and this has been followed in later years by the elaborations of Goldschmidt, Pauling, and Zachariasen. Using the figures for atomic size, and electrostatic energy considerations, Pauling has also deduced a set of rules of great importance in structure determination. Dr. Hassel's book deals with all these points, and with many more, of which the crystal chemistry of the silicates and of the intermetallic compounds may be mentioned.

The treatment throughout is simple and avoids all reference to the various technical methods of obtaining results. In this respect it is particularly valuable to physical chemists, particularly at a time when questions of atomic binding are receiving so much attention. It is a book to be read side by side with Sidgwick's *Covalent Link.* There are few illustrations, which is perhaps a pity, but this consideration was no doubt dictated by the fact that the book is one of a series.

J. T. RANDALL.

A STUDY OF THE ACTION OF ACIDS ON ZINC AT PRESSURES OF FROM ONE TO THIRTY THOUSAND ATMOSPHERES

THOS. C. POULTER AND GLEN E. FRAZER

Department of Physics, Iowa Wesleyan College, Mount Pleasant, Iowa

Received June 27, 1932

INTRODUCTION

While much of the data in this article is of a qualitative nature, the authors thought that the material was of sufficient interest to be published.

The importance of pressure as affecting chemical equilibrium has long been recognized, and many equilibrium conditions can be calculated to a high degree of accuracy. In many cases it is experimentally impossible to obtain the calculated conditions necessary for equilibrium. Such a case is that of the reaction of acids on zinc. The electrical potential exhibited by the zinc electrode as compared with that of hydrogen is a measure of the tendency of the reaction $H_2SO_4 + Zn \rightarrow ZnSO_4 + H_2$ to proceed in the direction indicated.

In order to calculate the pressure necessary to bring this reaction to equilibrium:

$$E = \frac{RT}{NF} \ln K = \frac{0.05915}{N} \log K \qquad E = 0.7581$$

$$1/2\ Zn + H^+ = 1/2\ H_2 + 1/2\ Zn^{++}$$

$$0.7581 = 0.05915 \log K = 0.05915 \log \frac{a_{Zn}^{\frac{1}{2}}\ P_{H_2}^{\frac{1}{2}}}{a_H}$$

from which we find that

$$K = 6.45 \times 10^{12}$$

If we have a solution containing zinc and hydrogen ions at unit activity and immerse in it a strip of pure zinc, it may be calculated from this value of the equilibrium constant that a pressure of 2.53×10^{25} atmospheres would be required to establish equilibrium.

The activity of the hydrogen ion has been studied as a function of hydrogen pressure by Hainsworth, Rowley, and MacInnes (3), and found to decrease by only 0.4 per cent at 500 atmospheres and 8.8 per cent at 1000 atmospheres.

The purpose of this investigation was to study the abnormal decrease in

the rate of reaction of acids on zinc reported by V. N. Ipatiev and his coworkers (4, 5) and also studied by F. E. Brown (2). Ipatiev and his coworkers reported that the velocity of this reaction is reduced to a small per cent of its normal value at pressures as low as 50 atmospheres and that equilibrium conditions are reached at less than 1000 atmospheres. A reversal of the reaction in some cases is reported.

APPARATUS AND PROCEDURE

A series of experiments was run by the authors in which the pressure measured was built up by the hydrogen evolved during the reaction. For

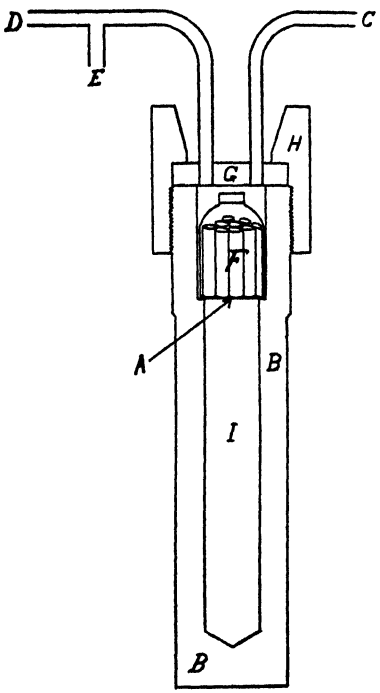

FIG. 1. PRESSURE REACTION BOMB

these experiments sticks of pure zinc, F, were placed in a very thin bottom glass container A (figure 1), the remaining space being filled with water. The top was then sealed with wax to prevent the acid from coming in contact with the zinc until it was desired to start the reaction. The glass container thus filled with zinc and water was supported on a shoulder in in the upper portion of the pressure bomb. The pressure bomb was lined with an acid-proof wax and filled with 6 *N* sulfuric acid. Two copper tubes were sealed through the cap, one of which led to a pressure gauge and the other to a hydraulic pump. The pressure could be released by means of a valve at E.

All of the copper tubing and the pressure gauge was filled with oil, leaving very little free space in the pressure system. After all materials had been placed in the bomb and the cap screwed in place, the zinc was brought into contact with the acid by jarring the bomb against a steel block, thus causing the zinc sticks to break through the thin bottom of the glass container. The pressure was read at intervals of half a minute. This assembly of apparatus permitted the reacting materials to be shaken at frequent intervals. The surface of the zinc sticks was scraped and rinsed with ether to remove all traces of dirt and grease.

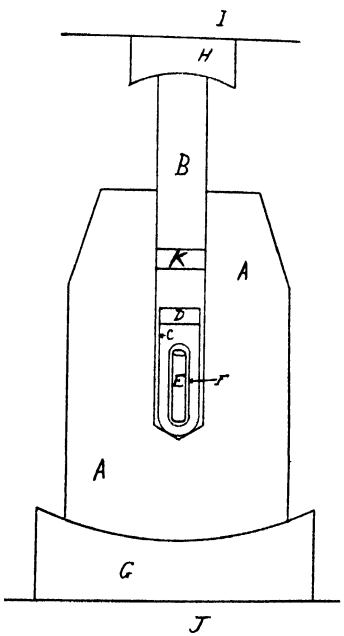

FIG. 2. PRESSURE CYLINDER

The pressure gauge employed in these experiments had a range of only 350 atmospheres. For the purpose of making the measurements at higher pressures a much heavier pressure bomb (figure 2), was constructed, which had an inside diameter of 15 mm. and a capacity of 17 cc. Leaking was prevented by placing a close fitting rubber stopper, K, in the cylinder ahead of the piston B. The curvature of the top of the piston and the bottom of the cylinder are sections of spheres having a common center for convenience in lining the cylinder up in the press. The blocks H and G rest directly in contact with the platens of the hydraulic press. The pressure on the reaction was determined as described in another article by one of the authors (6). For these experiments the zinc, E, was sealed in a glass

capsule, F, in order to prevent it from coming in contact with the acid until the assembly was completed. The acid, together with the capsule containing the zinc, was placed in a short rubber cup, C, which was stoppered and placed in the pressure cylinder.

The remaining free space was filled with a light paraffin oil. The glass capsules containing the zinc were broken at from 8000 to 12,000 atmospheres pressure. The zinc sticks which had been previously weighed were allowed to remain in contact with the acid for 30 minutes at 20°C. They were then removed as rapidly as possible, washed free from acid, dried, and

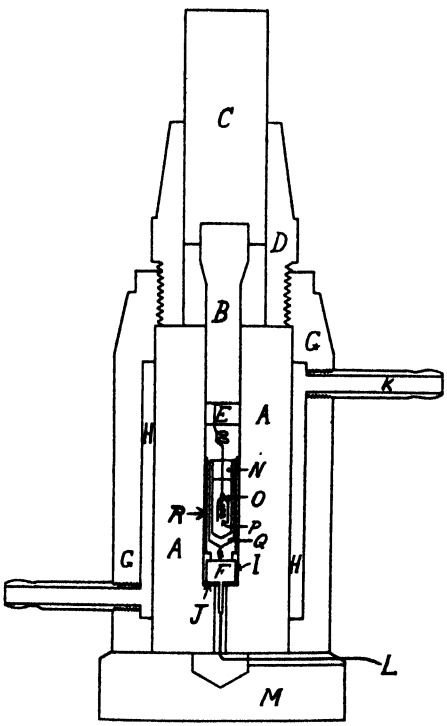

FIG. 3. PRESSURE CYLINDER

again weighed. The loss in weight could be thus determined for various pressures.

Attempts were made to measure the E. M. F. of a cell composed of the zinc and hydrogen electrodes in normal sulfuric acid. In order to do this it was necessary to construct a pressure cylinder in such a way that an electrode could be insulated through the wall of the cylinder and yet withstand the high pressures without leaking. For this purpose the pressure cylinder and cell assembly shown in figure 3 were constructed. The zinc electrode, Q, was made in the form of a cup into which the sulfuric acid was placed.

The platinized platinum electrode, P, was surrounded by a glass apron, 0 to prevent contact with the zinc electrode. It was held in place by a rubber stopper, N, inserted in the top of the zinc cup. A mica tube, R, prevented the zinc from coming in contact with the cylinder wall. The free space in the pressure cylinder was filled with a light paraffin oil and the pressure developed and measured as with the previous cylinder. This cylinder was equipped with a water jacket for temperature control. Water from a thermostat was circulated through the water jacket and the platens of the hydraulic press.

EXPERIMENTAL RESULTS

In the experiments where the evolved hydrogen was allowed to build up the pressure, about twenty minutes was required for pressures of 350 at-

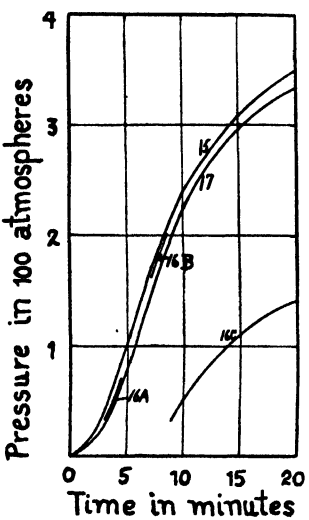

FIG. 4. TIME-PRESSURE CURVES

mospheres to be developed. A few typical pressure–time curves are shown in figure 4. In experiment No. 16 the initial conditions were made as nearly identical with those of No. 15 as possible. However, instead of allowing the reaction to take place under its own gradually increasing pressure, the pressure of the system was regulated as follows by means of an oil pump. The reaction was started at 34 atmospheres and the hydrogen allowed to build the pressure up to 68 atmospheres, at which time the pressure was raised by means of the pump to 163 atmospheres. The evolved hydrogen was then allowed to build the pressure up to 202 atmospheres. The pressure was then released to 34 atmospheres and allowed to build up to 116 atmospheres. The experiment was then discontinued after having extended over the same length of time as No. 15.

The reaction in the next pressure cylinder employed was followed by means of the loss in weight of the piece of zinc during the time it was in contact with the acid. The pieces of zinc were all 5 mm. in diameter and 25 mm. in length so as to expose the same surface to the acid. In all cases where the pressure was not higher than 8000 atmospheres the loss in weight of the zinc was from 0.5 to 1.0 g. These experiments were run at pressures of from 300 to 8000 atmospheres, and the loss in weight was found to be independent of the pressure. However, if the pressure was maintained at above 9000 atmospheres, the loss in weight of the zinc was never more than 0.02 g.

The assembly shown in figure 3 was then constructed and E.M.F. determinations were attempted, but with little success, particularly at the higher pressures as the results fluctuated over a large range. However, the quali-

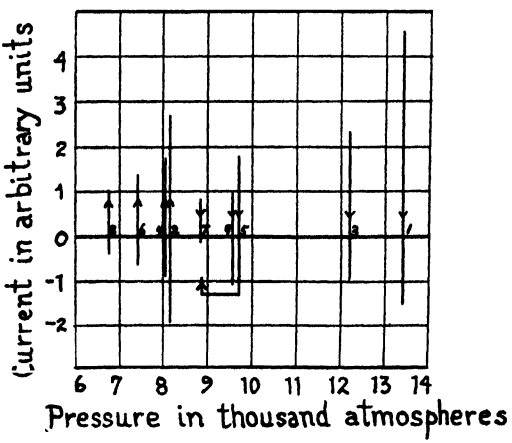

FIG. 5. REVERSAL OF CURRENT AT CONSTANT PRESSURE FOLLOWING A PRESSURE CHANGE

tative results proved to be very interesting. Since E.M.F. measurements were so unreliable, a galvanometer was substituted for the potentiometer. The pressure was then varied between 1 and 30,000 atmospheres. Between 8000 and 9000 atmospheres a marked increase in current was noticed, particularly if the pressure was raised rapidly. The current again returned to its normal value if the pressure was held constant at its new value. Above 9000 atmospheres the value of the current dropped almost to zero in those cases in which only a short time elapsed between the assembling of the cell and the attainment of this pressure. The value of the current remained at this low value as long as the pressure was maintained above 8900 atmospheres.

In cases where several minutes passed before a pressure of 9000 atmospheres was reached, the current dropped to zero and reversed direction,

and a small current was built up in the opposite direction. In such cases the original direction of the current was obtained by dropping the pressure to below 8400 atmospheres and was again reversed by raising it to above 8900 atmospheres. In one case the direction of the current was reversed nine times. Figure 5 shows the change in current following a change in pressure. The segments in this figure are numbered in the order in which they were obtained experimentally, and each segment represents the change in current at constant pressure but immediately following a pressure change. For instance, the pressure was built up to over 13,000 atmospheres, at which time the current changed as indicated by segment one; then the pressure was released to a little over 8000 and the current changed as indicated by segment two and so on. The pressure changes in each case were made rapidly from the pressure represented by the position of the previous segment of the curve. These measurements were made at 20°C.

The pressure at which reversal takes place depends upon the temperature. The reversal of current takes place at 7000 atmospheres if the temperature is 5°C.

In all cases following a reversal of current the odor of hydrogen sulfide was distinctly noticed upon opening the cylinder, but in cases where no reversal had occurred hydrogen sulfide was not detected.

No reversal was obtained if bright platinum was used instead of platinized platinum for the hydrogen electrode. Moreover, no reversal was obtained with either type of electrode if hydrochloric acid was used instead of sulfuric acid.

DISCUSSION OF RESULTS

At low pressure the evolution of hydrogen from the surface of a metal during the action of an acid upon it keeps the surface freed from material that would tend to prevent the acid from coming into contact with the metal surface and at the same time keeps the acid stirred.

If this same reaction is carried out under pressure, the hydrogen is almost, if not completely, dissolved in the acid as fast as it is formed and there are at most only a very few small bubbles produced. Therefore, little or no circulation occurs. It was found that a very slight trace of grease on the surface of the zinc, such as would be produced by handling with apparently clean hands, would cause a very marked retarding of the speed of reaction when the system was under pressure. The normal reactivity could be restored by washing the zinc in ether. Another effect directly due to lack of stirring is that of local decrease in acid concentration and in increase in salt concentration at the surface of the metal. The decided decrease in the slopes of the curves of figure 4 as the reaction proceeds are due largely to the change in concentration of the acid rather than to any

effect due directly to pressure. This is apparent from the curves for experiment No. 16 as shown in figure 4. If the velocity of the reaction were affected by pressure, the three segments of curve 16 should be parallel to those portions of number 15 corresponding to the same pressure, but since they are parallel to those portions corresponding to the same time position, it is apparent that pressures up to 350 atmospheres have little effect upon the reaction of sulfuric acid on zinc.

Ipatiev and his coworkers report that in some cases 122 days were required for the zinc–sulfuric acid system to build up a pressure of 350 atmospheres. That pressure was obtained by the authors with the same reactants within twenty minutes. The difference is likely, owing to the fact that the authors were able to fill all of the space in the container with liquid and that the surface of the zinc in the experiments herein described was free from all traces of grease, whereas Ipatiev took no such precautions. The authors were also able to shake the reacting materials at frequent intervals.

It was desired to investigate the effect of higher pressure upon the action of sulfuric acid in zinc, since no marked effects directly due to pressure had been observed up to 350 atmospheres.

The method of allowing the reaction products to build up the pressure does not lend itself to very accurate measurements, particularly when the pressure changes are large, because of the considerable time involved, the accompanying changes in concentration, and the change in volume of the system when the metal goes into solution in the form of its salt (5). Other factors are the penetration of hydrogen through the steel (1) and the compressibility of the heterogeneous system at high pressure. An attempt to correct for all of these factors would not lead to dependable results.

A more dependable method is that of measuring the decrease in weight of a piece of zinc of definite size and shape under controlled conditions.

While the activity of the hydrogen ion is reduced by 8.8 per cent at 1000 atmospheres of hydrogen pressure it might be supposed that the above reaction would be correspondingly slowed down; however, this decrease in activity is not a direct result of pressure, but is due to the solubility of hydrogen at that pressure, a condition which cannot be accomplished until after the reaction has proceeded for considerable time.

It is of interest that it is impossible under these conditions to acquire a higher concentration of dissolved hydrogen than that acquired at about 9000 atmospheres, because at that pressure hydrogen readily passes through the walls of a steel container.

The loss in weight of 0.02 g. or less for cases where the pressure was maintained above 9000 atmospheres can be accounted for by the time required to remove the zinc from the acid after releasing the pressure. The reason for the sudden decrease in the reaction at 9000 atmospheres is fairly

clear; at this pressure little or no loss in weight of zinc would be expected, since at pressures above 9000 atmospheres at 20°C. the solution solidifies, owing to the formation of ice VI, thus preventing the migration of the acid to the surface of the zinc.

The irregularity of the potential of the zinc–hydrogen cell is probably due to the irregularity of local concentration conditions around the electrode and the reduction of sulfuric acid to hydrogen sulfide at the platinized platinum electrode. This is indicated by the strong odor of hydrogen sulfide when the cells are opened. It also accounts for the reversal of the current at pressures above that necessary for the formation of ice VI. The fact that no reversal occurs when a bright platinum electrode is used or when hydrochloric acid is used instead of sulfuric acid also indicates that the reaction $4H_2 + H_2SO_4 \rightarrow H_2S + 4H_2O$ takes place at the surface of the platinized platinum electrode. The reaction is catalyzed by the platinized platinum and the high pressure. Because of the smaller volume of the products of this reaction it would be favored by pressure. The formation of hydrogen sulfide probably would not account for the reversal of polarity if it were not for the fact that the formation of hydrogen is practically stopped by the solidification of the acid solution.

As the pressure is quickly raised past that necessary for the formation of ice VI an increase in temperature occurs, owing to the change in volume. This would account for the sudden increase in current occurring at that pressure. Upon standing for a few minutes this heat energy is conducted through the cylinder walls and the solution solidifies owing to the formation of ice VI, whereupon the current drops to its low value. Further evidence that the acid solution is solidifying is the fact that the current is reversed by a pressure of 7000 atmospheres if a temperature of 5°C. is employed. A relatively large change in volume takes place within the same pressure range as the reversal of current, for further proof of the formation of a solid modification. These two pressures approximate those found by Bridgman for the formation of ice VI at the corresponding temperature.

SUMMARY

The velocity of the reaction $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$ is affected very little by pressure up to 8900 atmospheres. Between that pressure and 30,000 atmospheres very little reaction occurs, probably owing to the inability of the acid to migrate to the surface of the zinc and to local concentration effects. An electric cell having zinc and hydrogen electrodes has its polarity reversed by a pressure sufficient to form ice VI. At a pressure of 8900 atmospheres at 20°C. in the presence of platinized platinum the reaction $4H_2 + H_2SO_4 \rightarrow H_2S + H_2O$ is predominant so long as a hydrogen concentration remains.

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THE SYSTEM PYRIDINE–ACETIC ACID. III

Electrical Conductance

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In an earlier paper by one of the authors (5), the effect of temperature on the viscosity of mixtures of pyridine and acetic acid was reported. In this work it was found that this system showed a sharp maximum viscosity in the neighborhood of 80 mole per cent acetic acid, the maximum persisting at this same composition for temperatures as high as 80°C.

In a more recent paper by the present authors (6), the melting point–composition relations of this system were reported. The melting point–composition diagram shows evidence of the existence of two eutectic mixtures and two complexes. One complex, showing 50 mole per cent acetic acid, had a melting point of −48°C. The second complex had a composition between 80 and 85 mole per cent acetic acid, with an incongruent melting point above −43°C. The first of these complexes is in no way shown by the viscosity–composition curves for this system. The second complex occurs at a composition in the neighborhood of the mixture having maximum viscosity.

In view of this lack of agreement between the melting point and viscosity data for this system, we have measured the electrical conductance over the entire range of composition for this system, to determine if this property is related to either of the properties previously reported.

The value of conductance measurements as a criterion for complex formation has been discussed by Kendall and Booge (1). They state that a maximum conductance always occurs in the vicinity of that composition corresponding to an unstable complex compound. Sakhanov (3) has also used conductance data as a means of identifying complexes existing in various systems.

Conductance measurements have been made on this system by Trifonov and Cherbov (7) and by Sakhanov (4). Neither Trifonov and Cherbov's nor Sakhanov's data extend completely over the entire range of composition.

APPARATUS

Conductance measurements were made with the usual Wheatstone bridge assembly, supplied with alternating current at 1000 cycles per

second. The ear phones were tuned to the same frequency. The accuracy of the slide wire and resistances was checked by balancing resistances against each other. A cylindrical conductivity cell with freshly platinized platinum electrodes was used for all measurements.

TABLE 1

The specific conductance of pyridine and acetic acid mixtures

ACETIC ACID	SPECIFIC CONDUCTANCE × 10^3				
	At 0°C.	At 9 9°C.	At 19.9°C	At 29.9°C.	At 40 1°C.
mole per cent					
0.000	0 0012	0 0013	0 0014	0 0015	0.0021
12.247	0.0035	0.0042	0.0049	0.0053	0.0061
25 033	0.0134	0.0163	0.0200	0.0231	0.0266
37.414	0.0408	0 0524	0.0652	0.0791	0.0933
49 678	0.1781	0.2295	0.2863	0.3392	0.3946
55.220	0 3989	0.5039	0.6114	0.7162	0.8169
59.821	0.7770	0 9777	1 1784	1.3659	1.5443
64.990	1.3567	1 7229	2 0799	2 4101	2.7034
69.929	2.0486	2.6645	3 2647	3 8336	4 3376
73.948	2.6051	3.4749	4.3401	5.1716	5.9117
74.910	2.6549	3.5500	4.4440	5.3075	6.0935
76.877	2 8373	3.8440	4 8543	5.8382	6.7132
77.532	2 8816	3 9066	4.9499	5.9482	6.8794
78.883	2.9731	4 0611	5 1759	6 2468	7.3942
79.490	2 9948	4 1030	5.2383	6 3422	7.3530
79.924	3.0134	4.1361	5.3060	6.4160	7.4508
80.081	3 0230	4 1524	5 3174	6.4462	7.4962
80.991	3.0542	4.2158	5.4108	6 5817	7.6672
82.015	3.0643	4.2415	5.4636	6.6647	7 7802
82.980	3.0613	4 2420	5 4831	6.7071	7.8546
83.903	3.0517	4 2381	5.4612	6.6744	7.8131
84.782	3.0205	4.2308	5.4548	6.6949	7.8580
85.916	2.9600	4.1181	5.3405	6.5502	7.7088
87.599	2.8200	3.9066	5.0625	6.2048	7.2892
89.880	2.5089	3 4458	4.4552	5.4733	6.4327
91 225	2.2263	3.0467	3.9190	4.7933	5.6421
93 848	1.4791	1 9928	2.5335	3.0720	3.5845
97.356			0.4706	0 5715	0.6793
100 000			$0.0_{5}53$	$0.0_{7}46$	$0.0_{7}74$

MATERIALS

The pyridine and acetic acid used in these measurements were purified in the manner described in our previous paper (6). Conductivity water was prepared by redistillation of distilled water from acid potassium permanganate. A standard brand of C.P. potassium chloride, recrystallized from conductivity water and dried at 110°C. for twelve hours, was used for determining the cell constant.

METHOD

Mixtures covering the entire range of composition were made up by weight, with compositions expressed in mole per cent acetic acid.

The constancy of the cell characteristics was frequently checked during the conductance measurements. The cell plates were kept shorted at all times except while actual measurements were in progress, as recommended by Morgan and Lammert (2).

All bridge readings were taken as near the center of the bridge as possible.

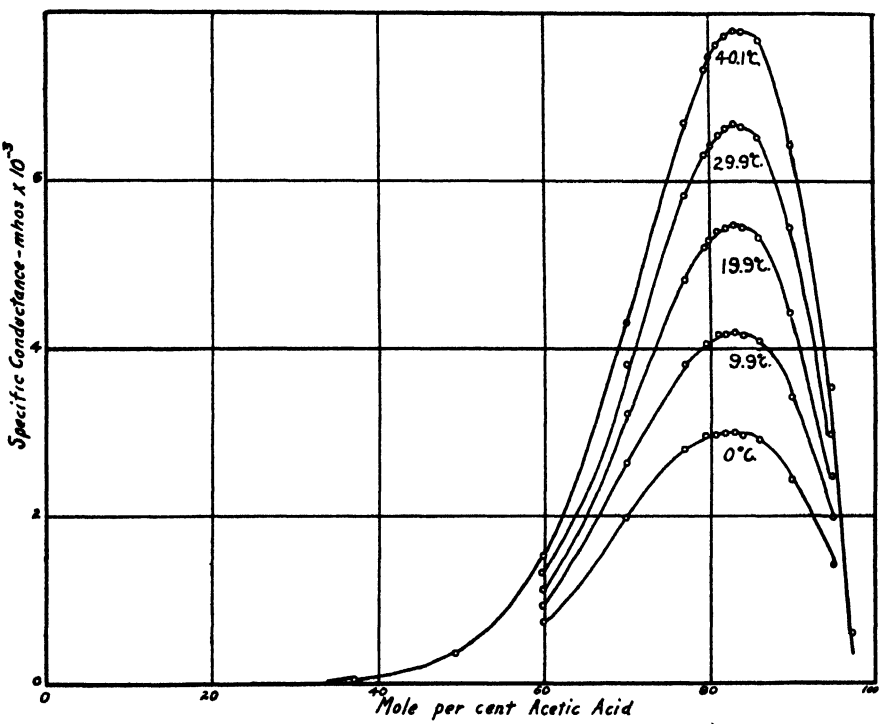

FIG. 1. SPECIFIC CONDUCTANCE ISOTHERMS FOR PYRIDINE–ACETIC ACID MIXTURES

Conductance measurements were made at 0, 9.9, 19.9, 29.9, and 40.1°C. These temperatures were maintained constant to within ±0.1°C.

EXPERIMENTAL RESULTS

Table 1 and figure 1 show the specific conductance of mixtures of pyridine and acetic acid over the entire range of composition for temperatures from 0°C. to 40.1°C. at approximately ten-degree intervals. The readings recorded are the average of several separate readings.

The specific conductance changes slightly, but regularly, with composi-

tion up to 50 mole per cent acetic acid. Above this composition, the specific conductance increases rapidly, reaching a pronounced maximum at about 83 mole per cent acetic acid. Beyond this concentration, the conductance drops rapidly to the low value for pure acetic acid. The position of the maximum remains practically constant over the temperature range investigated. The maximum is sharper at the higher temperatures.

There is no evidence of any irregularity in the specific conductance of this system at 50 mole per cent acetic acid, at which composition the melting point diagram indicates the existence of a complex. The sharp maximum in the conductance curve at 83 mole per cent acetic acid indicates, as do the viscosity and fusion point data, a complex of composition between 80 and 85 mole per cent acetic acid.

SUMMARY

The specific conductance of mixtures of pyridine and acetic acid has been measured over the entire range of composition.

The conductance data shows a single maximum at 83 mole per cent acetic acid, indicating a complex of this composition. This agrees with the viscosity data and in part with the melting point data for this system.

No evidence was obtained which would indicate the existence of a complex at 50 mole per cent acetic acid, as shown by the melting point data for this system.

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PHYSICOCHEMICAL STUDIES ON GUM ARABIC SOLUTIONS. III

Osmotic Pressures of Solutions of Arabic Acid and Sodium Arabate

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The manner in which diffusible ions will be found to be distributed at equilibrium on the two sides of a membrane, on one side of which there exists a colloid electrolyte (one ion non-diffusible), has been placed on a theoretical foundation by Donnan (5, 6, 7), and the theory has been confirmed by him and by others in numerous experiments. Donnan's theory goes further, however, and predicts that the equilibrium osmotic pressure shown by such a system should be proportional to the difference between the total moles of diffusible ions inside and outside the membrane, modified by any osmotic effect arising from the colloid micellae.

For example, in a system containing only hydrochloric acid and arabic acid, HAr, where the colloid is contained inside of a membrane which is permeable to H^+ and Cl^- ions but not permeable to the arabate ion or to the arabic acid molecule, at equilibrium the diffusible ions will be distributed in such a manner that

$$[H^+]_i \cdot [Cl^-]_i = [H^+]_o \cdot [Cl^-]_o$$

and

$$\frac{[H^+]_i}{[H^+]_o} = \frac{[Cl^-]_o}{[Cl^-]_i}$$

Also,

$$[H^+]_o = [Cl^-]_o$$

but

$$[H^+]_i > [Cl^-]_i$$

(Here [H], [Cl] etc. must signify activities of the respective ions, but will be very nearly equal to their concentrations when very dilute solutions are

employed.) These relationships have been experimentally shown to exist. The Donnan theory postulates, in addition, that the osmotic pressure which the solution inside the membrane will show, when in equilibrium with the solution outside, will be defined by the expression

$$\pi = RT\,[([H^+]_i + [Cl^-]_i + \Sigma\,[\text{Micellae}]) - ([H^+]_o + [Cl^-]_o)]$$

This relationship, of course, would hold if the membrane were impermeable to all the dissolved substances but permeable to water. However, when the only restraining force acting to prevent movement of the diffusible ions across the membrane is the electrostatic attraction which has caused their unequal distribution, as in the example given, experiments, from time to time, have indicated that there exists a difference between the observed osmotic pressure and that calculated on the basis of the Donnan theory.

In fact, Donnan and Harris (8) and Bayliss (2) found for solutions of Congo red that the observed osmotic pressure was only 87 to 94 per cent of that calculated on the assumption of a molecularly dispersed but unionized state of the dye. Donnan assumed the formation of aggregates of dye molecules to explain this discrepancy between observed and calculated osmotic pressures. Zsigmondy (15) measured, in addition, the conductivity of the colloid solution and concluded that the relationship existing between conductivity and osmotic properties, even with the assumption of the formation of a large colloidal ion, could not be explained on the basis of the older theories. He postulated that the discrepancy arises as a result of interionic forces in the manner pictured by the Debye-Hückel theory.

Loeb (11) studied the osmotic pressures of solutions of various proteins and found that the difference in concentration in crystalloid ions on the two sides of the membrane, at equilibrium set up as a result of the Donnan phenomena, could account completely for the osmotic pressure shown by a solution of casein chloride (12). In this case the colloid micelle was apparently so large that it exerted no measurable osmotic pressure itself. With gelatin chloride Loeb found that the osmotic pressure observed did not coincide with that calculated from the difference in ionic concentrations, although it varied in much the same manner with change in pH of the system. Loeb believed that the osmotic properties of protein solutions were completely defined by the Donnan hypothesis.

More recently Rona and Weber (13) have measured the activities of the diffusible ions and the osmotic pressure at equilibrium in the system, myogen chloride + HCl. They found the ratio $[H^+]_i/[H^+]_o$ to be equal to the ratio $[Cl^-]_o/[Cl^-]_i$, but found deviations between observed and calculated osmotic pressures similar to those which Loeb found with gelatin solutions. At low concentrations of hydrochloric acid (near isoelectric point of the protein) the measured osmotic pressure was greater

than that calculated on the basis of the measured diffusible ion distribution, while at higher hydrochloric acid concentrations the reverse was true. The former deviation was explained as due to the osmotic effect of the protein molecules themselves augmenting that of the diffusible ions. The latter deviation they picture as due to an influence of the large micellar ions exerted upon the osmotic activity of the small ions, which was noticeably different from (and greater than) their effect upon the electrode activity of the same ions.

E. Hammarsten (9) observed that the osmotic pressure exhibited by nucleic acid and Na_4-nucleate inside a collodion membrane, against distilled water on the outside, was less than that which the equilibrium distribution of small ions alone should show, also less than would be expected if no ionization occurred and the material were molecularly dispersed (calculated from the known molecular weight of the acid). He concluded, therefore, that some aggregation had taken place and that the small ions are active osmotically only to a small extent or not at all. This loss of osmotic activity of the small ions (which, however, still retain their activity at an electrode, since their concentrations were determined in this manner) he assumes to be due to an interionic influence resulting from the great difference in size of the colloid and crystalloid ions. In support of this explanation H. Hammarsten (10) found that the osmotic pressure of a solution of guanylic acid (ion of relatively small molecular weight) was that normally expected from the difference in total ionic concentration on the two sides of the membrane. (His calculations were made from the value of a maximum osmotic pressure observed after about six hours.) With salts of acids of higher molecular weight he confirmed the observations of E. Hammarsten. This anomalous osmotic effect, wherein the osmotic pressure of the colloid solution is less than would be calculated on the basis of the measured activities and distribution of the components present, has been called the "Hammarsten effect."

Bjerrum (3) measured the osmotic pressure, membrane potentials, and hydrogen-ion activity of solutions of chromium hydroxide and found that $P = P_1 + P_2$, where P was the observed pressure, P_1 was the osmotic pressure of the colloid particles (estimated to contain about one thousand chromium atoms), and P_2 was the osmotic pressure derived from the unequal distribution of ions on the two sides of the membrane. He found discrepancies between the observed membrane potentials and those calculated from osmotic pressure measurements, however, and believed this to be due to an unequal influence of the colloid upon the conductivity, electrode activity, and osmotic activity of ions adsorbed by it.

Samac, Knop, and Pankovic (14) measured osmotic pressures of an amylopectin (from potato starch), of lignosulfonic acid, and of an ammonium salt of humus (from peat) against water, using collodion sacs. They

found the observed osmotic pressures to be less in all cases than would be expected from the measured difference in concentration of the small ions alone and to be of the order of magnitude to be expected from the molecular weights of the colloids, calculated from other data, entirely neglecting any ionization. Their conclusion was that the small ions (*Gegenionen*) were osmotically inactive. Samac and Ribaric, however, had found that the freezing point lowering in a lignosulfonic acid solution was very close to that required on the basis of hydrogen-ion concentration alone.

Adair (1) studied the osmotic pressure of hemoglobin against distilled water and against solutions of diffusible salts. He measured, at the same time, the membrane potentials and distribution of diffusible ions. His conclusions were (a) that the relationships between diffusible ion activities and membrane potentials were in accord with the Donnan theory, (b) that within a limited range of hydrion, salt, and protein concentrations the observed osmotic pressure was equal to the sum of the pressure derived from the colloid, molecularly dispersed, and the pressure arising as a result of unequal distribution of diffusible ions on the two sides of the membrane, and (c) that the theory of Barcroft and Hill, which pictures a variable degree of aggregation of the colloid in explanation of the anomalies observed in its osmotic pressure relationships, was not correct. Adair claims the large deviations from the van't Hoff law to result from changes in activity of the protein molecule, this being a function of salt concentration, hydrion concentration, and protein concentration.

Thus, while discrepancies between theory and experimental results have been repeatedly indicated, no adequate study has been made of the phenomenon. This is probably due to the fact that most of such work has been done with colloids, the micellar weight of which was sufficiently small so that the osmotic pressure arising therefrom could not be neglected. This complication makes it almost impossible to obtain accurate measures of the deviation of the calculated and observable osmotic effects of the diffusible ions alone. In the experiments described below, using purified, electrodialyzed gum arabic, the colloid micella was apparently so large as to exert negligible osmotic pressure, and the relationships existing between observed and calculated osmotic pressures arising from the unequal distribution of diffusible ions alone became relatively easily apparent.

EXPERIMENTAL

The method for preparation of the colloid, gum arabic, and some of its physical properties have been described in the first paper of this series (4). In the experiments described in the present paper, only the sodium salt of the arabic acid was used. This salt contained 85×10^{-5} equivalents of Na per gram of dry colloid. The electrodialyzed arabic acid was neutralized with sodium hydroxide and the solution evaporated to dryness *in vacuo* at

70°C. The colloid was kept in the dry form and the solutions were prepared as needed. This colloid has properties which are very desirable for this type of experiment. It has no isoelectric point, acting as an anion at all values of pH; it is infinitely soluble in water; it does not easily hydrolyze in acid solutions and it requires no preservative to prevent bacterial hydrolysis.

The method used for measuring the osmotic pressure of the solutions was that of applying a constant pressure to the colloid solution inside of a sac-shaped membrane which was partially or wholly immersed in an external

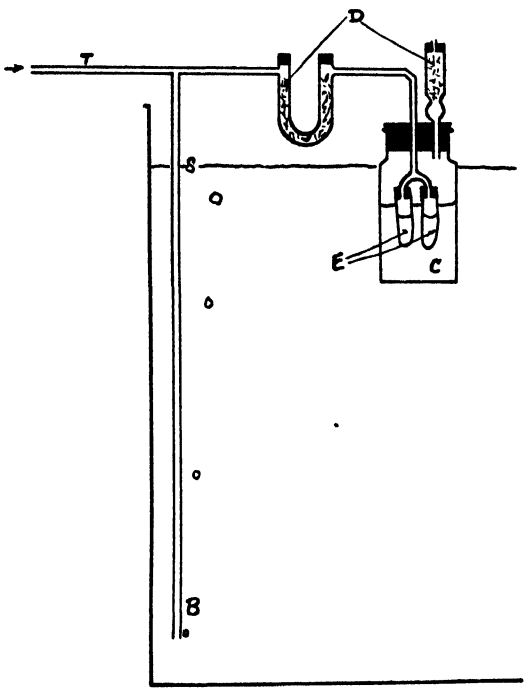

FIG. 1. DIAGRAMMATIC REPRESENTATION OF APPARATUS USED FOR OSMOTIC PRESSURE DETERMINATIONS

solution containing no colloid, until equilibrium was attained throughout the system. Figure 1 shows diagrammatically the apparatus used. The samples of colloid to be examined (in duplicate) were placed in collodion sacs (E) which were fastened by rubber bands to the tube through which constant pressure was applied. The applied constant pressure was obtained by slowly and continuously forcing air into the system at T and allowing it to escape at B, thereby displacing water in the tube between B and the surface of the liquid external to the tube. The pressure effective on the meniscus of the colloid solution in E would then be equal to the

column of water displaced in the tube (S to B) modified by the difference in the height of the menisci in E and in C. Most of the experiments were carried out when the pH was well on the acid side of neutrality in order to eliminate carbon dioxide adsorption. In those cases where neutrality was approached in the solutions, carbon dioxide adsorption was reduced to a minimum by protecting both sides of the system containing the colloid and external solutions by soda lime tubes (D). This protection was imperfect, however, and in a few cases where the external solutions were nearly neutral it is necessary to assume that some bicarbonate ion is present.

The final volume containing the colloid was determined by weighing the solution left inside the membrane at equilibrium. The observed (equilibrium) osmotic pressure, then, would be equal to the constant pressure applied. The final concentration of the colloid in solution could be calculated from the amount of colloid initially placed in the sac and its volume as determined from the final weight of the solution. The final volumes (V_i) used for the colloid solutions in the following tables of calculations are corrected for the weight of gum arabic present in each instance (i.e., $V_i = F - A$). V_i, therefore, signifies the volume of solvent left inside the membrane at equilibrium. The membranes used were made of collodion. They were prepared in the usual manner, no particular care being exercised as to uniformity of their preparation. The only care taken in their preparation was that required to get them thick enough to withstand the pressure applied and to prevent leaks, but not so thick or impermeable as to require too long a time for equilibrium to be reached. Equilibrium values obtained are independent of the pore radius and material of the membrane.

In all experiments the determinations were made in duplicate by placing equal amounts of colloid in two sacs which were then placed under the same pressure with a common external solution. A criterion for the attainment of equilibrium was as follows: Two equal samples of the colloid were weighed out and placed in the two collodion sacs. To one was added 10 cc. of distilled water. Both were then placed in the same external solution under the same pressure and allowed to stand. After about forty-eight hours the weights of solution inside of each sac had reached identical values. Since water moved out of one sac and was drawn into the other to reach the same final amount in each, this final value was a true equilibrium value. In all the experiments at least sixty hours were allowed for equilibrium to be attained.

In the tables the final weight of solution in each sac is given in the column designated by F; the weight of dry colloid contained in each is given in the column under A. Subsequent measurements of pH and all calculations are made upon the combined samples. In all experiments,

except those given in table 1, the measurements were carried out in individual 500-cc. bottles, as shown in figure 2.

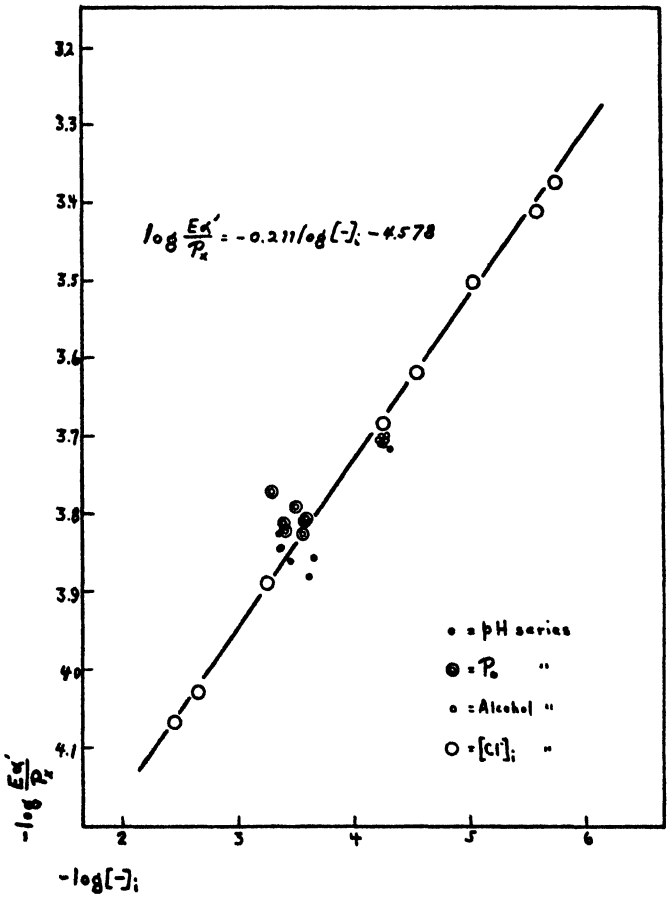

FIG. 2. GRAPH SHOWING THE MANNER IN WHICH THE FACTOR $E\alpha'/P_x$ VARIES WITH CHANGE IN CONCENTRATION OF FOREIGN SALT, $[-]_i$, IN THE COLLOID SOLUTION

E = the potential across the membrane which is impermeable to the colloid ion; α' = the number of equivalents of ions derived from one gram of the colloid; and $P_x = P_c - P_o$ is a measure of the deviation of the osmotic pressure calculated according to the Donnan hypothesis, P_c, from the observed equilibrium osmotic pressure, P_o, across the membrane. $[-]_i$ signifies the concentration of anions other than the colloid anion within the colloid-containing solution.

The volumes of solvent present in the internal (i) and external (o) solutions, at equilibrium, are given in the tables in the column designated as V, and the pressure against which equilibrium was attained, by P_0. All experiments were made at 25°C.

After equilibrium had been gained, the hydrogen-ion concentration was determined electrometrically (with the hydrogen electrode) on the inside and outside solutions. These measurements gave directly the difference in potential, E (millivolts), across the membrane, and from this could be calculated the ratio of distribution of hydrogen ions in the system. This ratio is shown in the tables as R. R = antilog ($E/59.1$).

The total equivalents of Na and Cl present in the system in each case are shown in the tables under columns headed by "Na" and "Cl," respectively. Since, according to Donnan's membrane equilibrium theory,

$$\frac{[H^+]_i}{[H^+]_o} = \frac{[Na^+]_i}{[Na^+]_o} = \frac{[Cl^-]_o}{[Cl^-]_i} = R$$

this value of R together with a knowledge of the volumes, V, inside and outside, and the total equivalents of each species of anion or cation present in the system, makes it possible to calculate the actual concentrations of each on both sides of the membrane. These values have been calculated assuming 100 per cent activity in all cases except where definitely indicated otherwise. The equilibrium concentrations of the various diffusible ions on the two sides of the membrane were calculated according to equations such as

$$[Na^+]_o = \frac{\text{Total Na (equiv.)}}{(R \cdot V_{i/1000}) + V_{o/1000}}, \quad [Na^+]_i = R \cdot [Na^+]_o$$

$$[Cl^-]_i = \frac{\text{Total Cl (equiv.)}}{(R \cdot V_{o/1000}) + V_{i/1000}}, \quad [Cl^-]_o = R \cdot [Cl^-]_i$$

where V_i and V_o = equilibrium volumes of solvent in cubic centimeters inside and outside, respectively.

The electrolyte concentration in all cases where 100 per cent ionization is assumed is of such a low order that the error so introduced is very small. In the tables, the concentrations of these ions are given under the heading $[Na^+]$, $[Cl^-]$, $[H^+]$, etc. and signify the concentration in equivalents per liter multiplied by 10^7. If the Donnan equilibrium theory holds in these cases, the total concentration of the positive ions should equal that of the total negative ions in the outside solution, where diffusible electrolytes alone are present. In the majority of cases this agreement is very close, and the conclusion is that the ions distribute themselves in accordance with the membrane equilibrium theory.

Knowing, now, the actual concentration (activities) of all ions on both sides of the membrane (neglecting, for the present, the colloid ion, since its molecular weight is high and unknown), the difference $[D]$, between their totals, $[T]$, inside and outside, will be a measure of the difference in their osmotic concentrations across the membrane. At 25°C. 1 mole of

dissolved material exerts an osmotic pressure equal to 25280 cm. of water. Then, $[D] \times 25280 \times 10^{-7}$ gives the effective osmotic pressure, P_c, in centimeters of water, exerted by the ions, assuming that the large colloid ion itself exerts no appreciable osmotic pressure and that it does not influence the osmotic activity of the small ions to a degree differing from its influence on the activity of these ions as determined electrometrically (i.e., from hydrogen-ion activity measured electrometrically and values calculated therefrom in the above outlined manner).

Examination of the tables reveals that in all cases the values of P_c are greater than the corresponding values of P_o, that is, the calculated osmotic pressure arising from the unequal distribution of the small ions alone is greater than the observed osmotic pressure. This is in accord with observations referred to above in the cases of certain other colloid solutions. Any osmotic pressure arising from the colloid ion itself would be in a direction such as to increase this difference. The value, $P_c - P_o = P_x$, is a measure of an anomalous equilibrium osmotic pressure of the colloid-containing system (continuing to neglect any possible osmotic pressure derived from the colloid itself).

In the experiment shown in table 1, the vessel used to contain the external solution was a tall glass cylinder. The external solution was common to all the sacs. Pressure was varied by placing the sacs at different levels below the surface of the liquid and applying an equal external pressure to all. The effective pressure then would be the difference between the applied pressure and the counter pressure exerted by the depths of water above the meniscus of the colloid solution in the sac, i.e., the weight of a column of water equal to the distance of this meniscus below the surface of the liquid in the containing cylinder.

For table 2 the variable was the pH. The total Cl content was kept constant in all the experiments and the pH varied individually by varying the relative amounts of NaCl and HCl added. In this case, and in all those in succeeding tables, the value of P_o was held nearly constant.

In the experiments shown in table 3, all variables were held constant except ethyl alcohol content, which was varied from 0.25×10^{-3} molar to 0.25 molar. This experiment was made in order to find out if diffusible non-electrolytes had any effect upon the osmotic properties of the colloid solution. These results serve, perhaps, to show the extremes of error in the determinations and in the calculated value of P_c. This is of the order of 10 per cent, the presence of the alcohol apparently having no effect upon the equilibrium attained.

Table 4 shows results obtained when the total Cl was changed from zero to 0.01 normal solution. In this case a mixture of 5 parts NaCl and 1 part HCl was added to the individual experiments in varying amounts so as to change the total Cl. The hydrochloric acid was added in order to

TABLE 1

Pressure varying; same external solution

NO.	SIDE OF MEMBRANE	IN TOTAL SOLUTION = 3000 CC. (i + o)		A	F	V	P_o	HYDROGEN-ION CONCENTRATION			E	R	$[Na^+] \times 10^7$	$[Cl^-] \times 10^7$	$[T] \times 10^7$	$[D] \times 10^7$	P_c	$P_c - P_o = P_z$	$\alpha' \times 10^4$	$\frac{E\alpha'}{P_z} \times 10^4$
		Cl	Na					E.M.F.	pH	$[H^+] \times 10^7$										
		equiv. $\times 10^3$	equiv. $\times 10^3$	grams	grams	cc.	cm. H_2O	mv.			mv.						cm. H_2O	cm H_2O		
1	i	4 513	2.550	0.100 0.100	5.201 5.029	10 030	14 5	405.8	2.722	18960	23 9	2 530	20050	6050	45060	14331	36 3	21 8	1 653	1 813
2	i	4.513	2 550	0.100 0 100	3 829 3 848	7 477	27 3	401.0	2 639	22950	28 7	3 061	24260	5000	52210	21481	54 2	26 9	1 577	1.682
3	i	4 513	2 550	0 150 0.150	4 865 4.840	9 405	37 8	397 3	2 578	26420	32 4	3 525	27930	4343	58693	27964	70 7	32.9	1.568	1.542
4	i	4 513	2.550	0 150 0 150	3.965 4 245	7 910	48 7	395 0	2 540	28830	34 7	3 847	30490	3980	63300	32571	82 4	33.7	1.460	1.520
5	i	4.513	2 550	0.200 0.200	3 850 3 836	7 296	85 7	389 4	2 443	36050	40 3	4 810	38110	3184	77344	46615	117.8	32.1	1.294	1.622
6	i	4.513	2.550	0.200 0.200	3 534 3 518	6 652	97 4	387 1	2 404	39430	42 6	5 260	41700	2914	84044	53315	134 8	37.4	1.302	1.482
7	i	4.513	2 550	0.300 0.300	4 961 4 915	9 276	110 5	385 5	2 377	41960	44 2	5 595	44350	2735	89045	58316	147.5	37 0	1.291	1.542
8	i	4.513	2 550	0 300 0.300	4 673 4.784	8 857	119 5	384 4	2 358	43830	45 3	5 850	46360	2617	92807	62078	157.1	37.6	1.292	1.567
	out					2933 1		429.7	3 125	7495			7924	15310	30729					

Legend for the tables: A = grams of arabate in sample. F = final weight of solution containing sample inside of membrane. V = volume of water at equilibrium on each side of membrane (in cc.). P_o = observed (or equilibrium) osmotic pressure (in cm. of water). $[H^+]$, $[Na^+]$, etc. = final concentration of diffusible ions (in equivalents per liter $\times 10^7$). E = membrane potential = $59.1 \times (pH_o - pH_i)$ (in millivolts). R = ratio of distribution of diffusible ions. $[T]$ = total concentration of diffusible ions (in equivalents per liter $\times 10^7$) on each side of membrane. $[D]$ = difference in concentration of diffusible ions (in equivalents per liter $\times 10^7$) across membrane. P_c = calculated osmotic pressure = $(D) \times 25280 \times 10^{-7}$ (in cm. of water). $P_z = P_c - P_o$. α' = equivalents ($\times 10^7$) of ions derived from 1 g. of colloid. $[-]_i = [Cl^-]_i + [HCO_3^-]_i$ (in equivalents per liter).

TABLE 2

Varying pH; total [Cl] constant; pressure constant

NO.	SIDE OF MEMBRANE	IN 320 CC. = TOTAL VOLUME OF SOLUTION (i + o) Cl	Na	A	F	V	P_o	HYDROGEN-ION CONCENTRATION EMF.	pH	$[H^+] \times 10^7$	E	R	$[Na^+] \times 10^7$	$[Cl^-] \times 10^7$	$[T] \times 10^7$	$[D] \times 10^7$	P_c	$P_c - P_o = P_x$	$\alpha' \times 10^4$	$\frac{E\alpha'}{P_x} \times 10^4$
		equiv. $\times 10^3$	equiv. $\times 10^3$	grams	grams	cc	cm H_2O	mv.			mv						cm. H_2O	cm H_2O		
1	i	0.680	0.340	0 200 0 200	2 589 2 583	4.77	127 1	379 4	2 273	53320	39 6	4 696	47320	4580	105220	62370	157 5	30 4	1 146	1.492
	o					314 83		419 0	2 945	11350			10080	21520	42850					
2	i	0 680	0 437	0 200 0.200	2 860 2 884	5 37	127 1	385 4	2 375	42170	40 1	4 786	61520	4505	108195	64955	164 2	37 1	1 331	1 440
	o					314 23		425 5	3 055	8810			12860	21520	43240					
3	i	0.680	0 534	0 200 0 200	3.161 3 235	6 00	127 6	393 8	2 519	30280	40 9	4 910	76400	4398	111078	67748	171.2	43 6	1 535	1.440
	o					313 60		434 7	3 210	6165			15565	21600	43330					
4	i	0 680	0 631	0.200 0 200	3 735 3 734	7 07	127 5	405 0	2 707	19630	42 0	5 166	93400	4191	117221	73691	186 2	58.7	1.922	1.377
	o					312 53		447 0	3 420	3800			18080	21650	43530					
5	i	0 680	0 728	0 200 0 200	4 567 4 742	8 91	128 1	422 5	3 003	9930	43 3	5 392	109470	4039	123439	79528	201 0	72 9	2 570	1.526
	o					310 69		465 8	3.735	1841			20300	21770	43911					
6	i	0 680	0 826	0 200 0 200	5 488 5 403	10 49	128 8	445 5	3 391	4062	46 5	6 150	136000	3558	143620	98970	250.0	121 2	3 580	1 375
	o					309 11		492 0	4 180	660 5			22110	21880	44650					
7	i	0.680	0 923	0 200 0 200	6.495 6 520	12 62	129 5	483 1	4 030	933 0	55 9	8 810	194500	2503	197936	153700	388 3	258 8	6 090	1 317
	o					306 98		539 0	4 975	105 9			22060	22070	44236					
8	i	0.680	0.1020	0 200 0.200	7.288 7 272	14.16	129 0	587 4	5 793	16 10	59 2	10 08	229500	2200	231700	186770	472 0	343 0	8.050	1.392
	o					305.44		646 6	6.797	1.596			22750	22180	44930					

TABLE 3

Alcohol varying; [Cl] constant; pressure constant; [Na] constant

NO.	SIDE OF MEMBRANE	IN 320 CC. = TOTAL VOLUME OF SOLUTION (i + o) Cl	Na	$[C_2H_5OH] \times 10^3$	A	F	V	P_o	HYDROGEN-ION CONCENTRATION E.M.F.	pH	$[H^+] \times 10^7$	E	R	$[Na^+] \times 10^7$	$[Cl^-] \times 10^7$	$[T] \times 10^7$	$[D] \times 10^7$	P_c	$P_c - P_o = P_x$	$\alpha' \times 10^4$	$\frac{E\alpha'}{P_x} \times 10^4$
		equiv. $\times 10^3$	equiv. $\times 10^3$		grams	grams	cc.	cm. H_2O	mv.			mv.						cm. H_2O	cm. H_2O		
1	i	0.3128	0.5930	0.25	0.2008	8.3808	16.36	130.2	511.3	4.505	312.5	75.0	18.52	181300	555.5	182200	162100	410.0	279.8	7.41	1.987
	o				0.2008	8.3828	303.2		586.3	5.773	16.86			9790	10280	20100					
2	i	0.3128	0.5930	0.50	0.2008	8.4498	16.46	130.2	512.7	4.530	295.0	73.6	17.50	175500	587.0	176400	155800	394.0	263.8	7.21	2.010
	o				0.2008	8.4108	303.1		586.3	5.773	16.86			10300	10280	20600					
3	i	0.3128	0.5930	5.00	0.2008	8.3538	16.24	129.8	510.8	4.500	316.2	72.5	16.80	172800	611.0	173700	153100	387.0	257.2	7.00	1.974
	o				0.2008	8.2888	303.4		583.3	5.725	18.82			10295	10270	20600					
4	i	0.3128	0.5930	10.00	0.2008	8.3888	16.34	130.2	509.4	4.475	335.0	74.9	18.76	182400	548.0	183300	163300	413.0	282.8	7.43	1.971
	o				0.2008	8.3568	303.3		584.8	5.748	17.86			9725	10290	20000					
5	i	0.3128	0.5930	25.00	0.2008	8.4428	16.41	130.2	511.1	4.502	314.7	75.2	18.66	181500	551.0	182400	162400	410.5	280.3	7.43	1.995
	o				0.2008	8.3708	303.2		586.3	5.773	16.86			9730	10280	20000					
6	i	0.3128	0.5930	50.00	0.2008	8.3598	16.23	129.9	510.9	4.500	316.2	73.7	16.95	173750	607.0	174700	154200	390.0	260.1	7.04	1.995
	o				0.2008	8.2738	303.4		583.6	5.730	18.65			10250	10280	20500					
7	i	0.3128	0.5930	250.00	0.2008	8.5198	16.68	127.2	513.9	4.549	282.3	74.6	18.23	178100	565.0	178900	158800	401.5	274.3	7.42	2.018
	o				0.2008	8.5048	302.9		588.5	5.810	15.48			9770	10300	20100					
8	i	0.3128	0.5930	800.00	0.2008	8.2248	16.14	127.6	511.1	4.502	314.7	77.6	20.54	192700	501.0	193500	173900	439.6	312.0	7.77	1.930
	o				0.2008	8.1948	303.8		588.7	5.815	15.31			9340	10270	19600					

TABLE 4

[Cl] varying; pressure constant

NO	SIDE OF MEMBRANE	IN 320 CC. = TOTAL SOLUTION (i + o)										HYDROGEN-ION CONCENTRATION																	
		Cl	Activity coefficient of NaCl γ	$\gamma \times$ Cl	Na	$\gamma \times$ Na	A	F	V	P_o	EMF	pH	$[H^+] \times 10^7$	E	R	$[Na^+] \times 10^7$	$[Cl^-] \times 10^7$	$[HCO_3^-] \times 10^7$	$[T] \times 10^7$	$[D] \times 10^7$	P_c	$P_o - P_o = P_z$	$\alpha' \times 10^4$	$\frac{E\alpha'}{P_z} \times 10^4$	$-\text{Log}\frac{E\alpha'}{P_z}$	$-\text{Log}[-]_1$	$[-]_1^{0.211}$	$\frac{E\alpha'[-]_1^{0.211}}{P_z} \times 10^4$
		equiv $\times 10^3$		equiv $\times 10^3$	equiv $\times 10^3$	equiv. $\times 10^3$	grams	grams	c	cm H_2O	mv			mv							cm. H_2O	cm H_2O						
1	i						0 150	8 207	16 142	131 5	558 6	5 305	49 52	114 4	86 50	129800		17 4	129865	126865	320 5	189 0	6 99	4 230	3 374	5 759	0 06240	2 640
	o				0 2550	0 2550	0 150	8 235	303 56		673 0	7 242	0 5725			1500		1500	3000									
2	i	0 032	0 993	0 0318	0 2817	0 2796	0 150	8 137	15 962	130 8	552 7	5 206	62 20	111 0	75 15	139800	13 34	11 45	139887	136163	344 1	213 3	7 44	3 880	3 411	5 605	0 06645	2 580
	o						0 150	8 125	303 74		663 7	7 082	0 8275			1861	1003	860	3724									
3	i	0 096	0 988	0 0948	0 3350	0 3310	0 150	7 669	14 970	131 5	548 2	5 130	74 10	94 8	39 90	146300	77 9	14 1	146460	139120	351 5	220 0	7 30	3 146	3 500	5 036	0 08750	2 754
	o						0 150	7 601	304 73		643 0	6 731	1 857			3670	3110	560	7340									
4	i	0 224	0 983	0 2202	0 4841	0 4760	0 175	8 089	15 703	131 2	526 2	4 767	171 0	81 5	23 40	165950	309		166340	152020	381 9	250 7	7 45	2 421	3 616	4 510	0 11280	2.733
	o						0 175	7 964	303 95		607 7	6 136	7 310			7090	7230		14320									
5	i	0 320	0 977	0 3128	0 6066	0 5930	0 200	8 626	16 804	131 0	518 2	4 629	235 0	74 4	18 12	177000	568		177800	157720	398 5	267 5	7 42	2 065	3 685	4 245	0 12820	2 646
	o						0 200	8 578	302 80		593 0	5 887	12 97			9770	10300		20080									
6	i	0 960	0 960	0 9220	1 1825	1 1360	0 225	6 456	12 499	130 4	464 8	3 720	1905 0	43 2	5 373	163200	5540		170650	110170	278 4	148 0	4 44	1 295	3 887	3 246	0 20800	2 692
	o						0 225	6 493	307 05		508 0	4 450	354 7			30360	29770		60480									
7	i	2 240	0 936	2 0970	2 3760	2 2240	0 300	5 401	10 168	130 4	429 2	3 115	7672 0	27 2	2 898	190400	23130		221200	85820	217 0	86 6	2 97	0 932	4 031	2 636	0 27920	2 602
	o						0 300	5 367	309 23		456 4	3 577	2648 0			65680	67050		135380									
8	i	3 200	0 922	2 9500	3 2610	3 0080	0 350	5 077	9 344	130 1	417 6	2 920	12020 0	22 2	2 378	215300	39530		266850	77200	195 2	65 1	2 51	0 854	4 068	2 403	0 31260	2 670
	o								309 96		439 8	3 296	5056 0			90600	94000		189650									

keep the pH on the acid side of neutrality and minimize carbon dioxide absorption. In this table the activity coefficients of sodium chloride were used to calculate the active concentration of Na^+ and Cl^- ions present, i.e., 100 per cent activity was not assumed. This use of the activity coefficients of sodium chloride is not entirely correct (not all the electrolyte was sodium chloride), but serves to give a somewhat closer approximation to the actual conditions than if 100 per cent activity were assumed. While not shown in the table, the chloride ion concentrations were determined electrometrically with the silver–silver chloride electrode in the external solution and were found to agree closely with the calculated values given. The agreement for the inside solutions was not good, especially at low chloride concentrations, the electrode measurements indicating concentrations which were somewhat higher than the calculated values given in the table. This was probably due to a fault in the electrode, since others have found the $[H^+]_i/[H^+]_o$ ratio to equal the $Cl[^-]_o/[Cl^-]_i$ ratio as required by the Donnan theory.

Analysis of these data shows, empirically, that the factor $E\alpha'/P_x$ is essentially a constant in those cases (tables 1, 2, and 3) in which the foreign salt concentration (as measured in terms of $[-]_i$, the total negative ion concentration inside the membrane other than the colloid ion itself) does not vary radically. The factor E is the membrane potential as obtained from the pH measurements, and $P_x = P_c - P_o$ and is a measure of the anomalous pressure found. The factor, α', signifies the equivalents of sodium and hydrogen derived from one gram of the colloid. The final gram concentration of the colloid being equal in each case to $A/V_i \cdot 1000$ and the equivalent concentration of the ions derived from the colloid being equal to $[H^+]_i + [Na^+]_i - [Cl^-]_i$, the volume of α' is given by the equation

$$\alpha' = \frac{[H^+]_i + [Na^+]_i - [Cl^-]_i}{A/V_i \cdot 1000}$$

When, however, the foreign salt concentration, $[-]_i$, is changed radically, as in table 4, the value $E\alpha'/P_x$ is no longer a constant. Figure 2 shows that the value $E\alpha'/P_x$ varies with the factor $[-]_i$ in a log-log ratio. Graphic solution of the curve so obtained gives the equation

$$\log \frac{E\alpha'}{P_x} = -0.211 \log [-]_i - 4.578$$

Thus it appears that the value

$$\frac{E\alpha'[-]_i^{0.211}}{P_x}$$

is a constant when, other than the colloid, only monovalent cations and anions are present in the system. This factor does not vary with concentration of colloid, salt, or pH.

SUMMARY

A method is outlined by which accurate osmotic pressure concentration relationships may be obtained for systems containing a colloid as the non-diffusible component.

Osmotic pressure measurements made on solutions containing arabic acid and sodium arabate show that the equilibrium distribution of water and diffusible ions across the membrane is independent of the size of pore and of the material of the membrane.

The equilibrium distribution of diffusible ions across the membrane is in accord with the Donnan membrane equilibrium theory.

The osmotic pressure, *calculated* on the basis of unequal distribution of diffusible ions and the Donnan theory, is consistently greater than the *observed* equilibrium pressure.

The difference between the observed and calculated osmotic pressures ($P_c - P_o = P_z$) bears a definite relationship to certain other variables in the system such that

$$\frac{E\alpha'[-]_i^{0.211}}{P_z} = \text{constant}$$

This factor remains constant through all changes in pH, sodium chloride concentration, and colloid concentration in the system. In this factor, obtained empirically, E represents the potential existing at equilibrium across the membrane, α' is a measure of the number of equivalents of small diffusible ions (*Gegenionen*) derived from unit weight of the colloid, and $[-]_i$ is a measure of the concentration of salt inside the membrane other than the colloid itself.

Diffusible non-electrolytes (ethyl alcohol), in concentrations up to 0.5 molar solution, exert no influence upon this relationship.

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ACTIVITY COEFFICIENTS IN MIXED SOLUTIONS AND THE GIBBS-DUHEM AND DUHEM-MARGULES FORMULAS

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For a one-phase system consisting of a solvent (component 1) and $(x-1)$ solute species (components $2, 3 \ldots x$) the so-called Gibbs-Duhem formula would commonly be written as follows:

$$\sum_{i=1}^{i=x} n_i \cdot \mathrm{d}\mu_i = 0 \tag{1}$$

n_i is the number of moles of constituent i, μ_i the chemical potential of that constituent. Equation 1 is a particular case of the more general thermodynamic relation:

$$-S \cdot \mathrm{d}T + V \cdot \mathrm{d}P - \sum_i n_i \cdot \mathrm{d}\mu_i = 0 \tag{2}$$

where the symbols S, T, V, P have their usual meaning. Equation 1 rules any variation of composition taking place at constant pressure and temperature. The proof of the Gibbs-Duhem formula is based upon the fact that the dependence of the chemical potentials μ_i (like that of all partial molar quantities) on composition only involves the mole fractions of the various constituents. In other words the various μ_i's are homogeneous and of degree zero in terms of the n_i's. Euler's theorem on homogeneous functions gives then, for the chemical potential μ_i (1, 7)

$$\sum_{j=1}^{j=x} n_j \frac{\partial \mu_i}{\partial n_j} = 0 \tag{2}$$

There are x relations of this type ($i = 1, 2, \ldots x$). The partial derivatives are taken at T, P, and all n_i's except n_j, constant. Applying now the well-known reciprocity relations:

$$\frac{\partial \mu_i}{\partial n_j} = \frac{\partial \mu_j}{\partial n_i} = \frac{\partial^2 F}{\partial n_i \partial n_j} \tag{3}$$

F being the free energy of the system, we may transform the set of equations 2 into the equivalent set of x equations:

$$\sum_{j=1}^{j=x} n_j \cdot \frac{\partial \mu_j}{\partial n_i} = 0 \tag{4}$$

In the particular case of two constituents the set 2 becomes:

$$n_1 \cdot \frac{\partial \mu_1}{\partial n_1} + n_2 \cdot \frac{\partial \mu_1}{\partial n_2} = 0 \tag{2.1}$$

$$n_1 \cdot \frac{\partial \mu_2}{\partial n_1} + n_2 \cdot \frac{\partial \mu_2}{\partial n_2} = 0 \tag{2.2}$$

The reciprocity relations 3 reduce to:

$$\frac{\partial \mu_1}{\partial n_2} = \frac{\partial \mu_2}{\partial n_1} \tag{3 1}$$

and the set 4 becomes:

$$n_1 \cdot \frac{\partial \mu_1}{\partial n_1} + n_2 \cdot \frac{\partial \mu_2}{\partial n_1} = 0 \tag{4.1}$$

$$n_1 \cdot \frac{\partial \mu_1}{\partial n_2} + n_2 \cdot \frac{\partial \mu_2}{\partial n_2} = 0 \tag{4.2}$$

We thus have as many equations of the Gibbs-Duhem type as there are components. These equations assume the form 2 or the form 4. Each set contains a total number of x^2 partial derivatives of the type $\frac{\partial \mu_i}{\partial n_j}$. The chemical potentials μ_i are of the form (1, 2)

$$\mu_i = \mu_i^0(T, P) + RT \cdot \log N_i f_i \tag{5}$$

μ_i^0 is a function of T and P only, R is the molar gas constant, N_i is the mole fraction and f_i the activity coefficient of the constituent i. We have (writing $\Sigma n_i = n$):

$$\frac{\partial \mu_i}{\partial n_i} = \frac{RT}{N_i} \cdot \frac{n - n_i}{n^2} + RT \cdot \frac{\partial \log f_i}{\partial n_i} \tag{6.1}$$

$$\frac{\partial \mu_i}{\partial n_j} = \frac{RT}{N_i} \cdot \frac{-n_i}{n^2} + RT \cdot \frac{\partial \log f_i}{\partial n_j} \tag{6.2}$$

The sets of equations 2 and 4 thus become:

$$\sum_{j=1}^{j=x} n_j \cdot \frac{\partial \log f_i}{\partial n_j} = 0 \qquad (i = 1, 2, \cdots x) \tag{7}$$

$$\sum_{j=1}^{j=x} n_j \cdot \frac{\partial \log f_j}{\partial n_i} = 0 \qquad (i = 1, 2, \cdots x) \tag{8}$$

In the particular case of two components these equations become:

$$n_1 \frac{\partial \log f_1}{\partial n_1} + n_2 \frac{\partial \log f_1}{\partial n_2} = 0 \tag{7.1}$$

$$n_1 \frac{\partial \log f_2}{\partial n_1} + n_2 \frac{\partial \log f_2}{\partial n_2} = 0 \tag{7.2}$$

and

$$n_1 \cdot \frac{\partial \log f_1}{\partial n_1} + n_2 \cdot \frac{\partial \log f_2}{\partial n_1} = 0 \tag{8.1}$$

$$n_1 \cdot \frac{\partial \log f_1}{\partial n_2} + n_2 \cdot \frac{\partial \log f_2}{\partial n_2} = 0 \tag{8.2}$$

The reciprocity relations 3 lead to analogous relations between the activity coefficients:

$$\frac{\partial \log f_i}{\partial n_j} = \frac{\partial \log f_j}{\partial n_i} \tag{9}$$

For a two-component system:

$$\frac{\partial \log f_1}{\partial n_2} = \frac{\partial \log f_2}{\partial n_1} \tag{9.1}$$

Besides the equations 7 or 8 we have the reciprocity relations 9 between the x^2 partial derivatives $\frac{\partial \log f_i}{\partial n_j}$. The number of distinct reciprocity relations is $\frac{x(x-1)}{2}$. (One differentiates each $\log f_i$ with respect to all the n_j's except n_i; each of the corresponding relations appears twice in the list.)

The total number of relations between the x^2 partial derivatives is thus:

$$x + \frac{x(x-1)}{2} = \frac{x(x+1)}{2} \tag{10}$$

In order to know all the partial derivatives in terms of all the n_i's we need

$$x^2 - \frac{x(x+1)}{2} = \frac{x(x-1)}{2} \tag{11}$$

non-thermodynamic relations. (Relations obtained in non-thermodynamic theories such as that of electrolytes; empirical relations deduced

from experimental data.) When all the $\frac{\partial \log f_i}{\partial n_j}$ of constituent i are known in terms of the various n_j's the total differential of $\log f_i$

$$d \log f_i = \sum_{j=1}^{j=x} \frac{\partial \log f_i}{\partial n_j} \cdot dn_j \tag{15}$$

is known.

Formula 15 is an exact differential since, on account of the reciprocity relations 9,

$$\frac{\partial^2 \log f_i}{\partial n_k \cdot \partial n_j} = \frac{\partial^2 \log f_j}{\partial n_k \cdot \partial n_i} \tag{16}$$

or

$$\frac{\partial}{\partial n_k}\left(\frac{\partial \log f_i}{\partial n_j}\right) = \frac{\partial}{\partial n_j}\left(\frac{\partial \log f_i}{\partial n_k}\right) \tag{17}$$

$\log f_i$ is then obtained by means of quadratures:

$$\log f_i = \varphi_i(n_1 \cdots n_j \cdots n_x) + \text{Constant} \tag{18}$$

The constant is determined by making a suitable assumption concerning a particular composition of the solution; for instance one assumes that $f_i = 1$ at infinite dilution (all n_j's, except n_1, equal to zero).

Attempts in the literature (5, 6, 7) to introduce the mole fractions N_i instead of the numbers of moles n_i in formulas 2 and 4 or in 7 and 8 have often led to incorrect equations. Dividing formulas 2 and 4 by n we obtain:

$$\sum_{j=1}^{j=x} N_j \cdot \frac{\partial \mu_i}{\partial n_j} = 0 \tag{19}$$

$$\sum_{j=1}^{j=x} N_j \cdot \frac{\partial \mu_j}{\partial n_i} = 0 \tag{20}$$

Formula 20 is often incorrectly written:

$$\sum_{j=1}^{j=x} N_j \cdot \frac{\partial \mu_j}{\partial N_i} = 0 \tag{21}$$

For the particular case of a two-component system formula 21 becomes:

$$N_1 \cdot \frac{\partial \mu_1}{\partial N_1} + N_2 \cdot \frac{\partial \mu_2}{\partial N_1} = 0 \tag{22}$$

It is however obvious, if one refers to equation 1, that the correct way of writing 22 is

$$N_1 \cdot \frac{d\mu_1}{dN_1} + N_2 \cdot \frac{d\mu_2}{dN_1} = 0 \tag{23}$$

and in general:

$$\sum_{j=1}^{j=x} N_j \cdot \frac{d\mu_j}{dN_i} = 0 \tag{24}$$

Formula 24 could be considered as the correct general form of the Duhem-Margules formula. For ideal systems it reduces to an identity. For non-ideal systems it becomes:

$$\sum_{j=1}^{j=x} N_j \cdot \frac{d \log f_j}{dN_i} = 0 \tag{25}$$

The confusion between formulas 22 and 23 has already been pointed out by Lecat (4).

Example 1. If $x = 2$ we need one non-thermodynamic relation: for instance, the dependence of $\log f_1$ or of the osmotic coefficient of the solvent on composition, as deduced from freezing point data. Such data will usually give $\frac{\partial \log f_1}{\partial n_2}$. Introducing the osmotic coefficient g_1, we make use of the relation:

$$\log f_1 = (g_1 - 1) \cdot \log N_1 \tag{26}$$

Differentiating with respect to n_2:

$$\frac{\partial \log f_1}{\partial n_2} = \log N_1 \cdot \frac{\partial g_1}{\partial n_2} - \frac{g_1 - 1}{n_1 + n_2} \tag{27}$$

Equations 7, 8, and 9 give:

$$\frac{\partial \log f_1}{\partial n_1} = -\frac{n_2}{n_1} \cdot \log N_1 \cdot \frac{\partial g_1}{\partial n_2} + \frac{n_2}{n_1(n_1 + n_2)} \cdot (g_1 - 1) \tag{28}$$

$$\frac{\partial \log f_2}{\partial n_1} = \frac{\partial \log f_1}{\partial n_2} = \log N_1 \cdot \frac{\partial g_1}{\partial n_2} - \frac{g_1 - 1}{n_1 + n_2} \tag{29}$$

$$\frac{\partial \log f_2}{\partial n_2} = -\frac{n_1}{n_2} \cdot \log N_1 \cdot \frac{\partial g_1}{\partial n_2} + \frac{n_1}{n_2(n_1 + n_2)} \cdot (g_1 - 1) \tag{30}$$

The total differential of $\log f_2$ is then:

$$d \log f_2 = \left[\log N_1 \cdot \frac{\partial g_1}{\partial n_2} - \frac{g_1 - 1}{n_1 + n_2}\right] dn_1 + \left[-\frac{n_1}{n_2} \cdot \log N_1 \cdot \frac{\partial g_1}{\partial n_2} + \frac{n_1(g_1 - 1)}{n_2(n_1 + n_2)}\right] \cdot dn_2 \tag{31}$$

Assuming that $\log f_2$ is zero when $n_2 = 0$, the integration from $n_2 = 0$ to n_2 at n_1 constant gives:

$$\log f_2 = -\int_0^{n_2} \frac{n_1}{n_2} \cdot \log N_1 \cdot \frac{\partial g_1}{\partial n_2} \cdot dn_2 + \int_0^{n_2} \frac{n_1(g_1 - 1)}{n_2(n_1 + n_2)} \cdot dn_2 \tag{32}$$

In the same way we have:

$$d \log f_1 = \left[-\frac{n_2}{n_1} \cdot \log N_1 \cdot \frac{\partial g_1}{\partial n_2} + \frac{n_2}{n_1(n_1 + n_2)} \cdot (g_1 - 1) \right] dn_1 + \left[\log N_1 \cdot \frac{\partial g_1}{\partial n_2} - \frac{g_1 - 1}{n_1 + n_2} \right] dn_2 \tag{33}$$

Assuming that $\log f_1$ is zero when $n_2 = 0$ and integrating from $n_2 = 0$ to n_2 at n_1 constant we have:

$$\log f_1 = \int_0^{n_2} \log N_1 \cdot \frac{\partial g_1}{\partial n_2} dn_2 - \int_0^{n_2} \frac{g_1 - 1}{n_1 + n_2} dn_2 \tag{34}$$

In both 31 and 33 $\frac{\partial g_1}{\partial n_2} dn_2$ may be replaced by dg_1, since n_1 is constant. In practice one takes n_1 equal to the number of moles corresponding to 1000 grams of solvent.

In the case of an electrolyte we may use the Debye-Hückel law for the activity coefficient. We thus have $\frac{\partial \log f_2}{\partial n_2}$ at n_1 constant. Thermodynamics gives then $\frac{\partial \log f_2}{\partial n_1}$, $\frac{\partial \log f_1}{\partial n_1}$, and $\frac{\partial \log f_1}{\partial n_2}$.

Example 2. If $x = 3$, there are two solute species and we need three non-thermodynamic relations. In the case of two dilute electrolytes the Debye-Hückel theory gives:

$$\frac{\partial \log f_2}{\partial n_2}, \quad \frac{\partial \log f_3}{\partial n_3}, \text{ and } \frac{\partial \log f_2}{\partial n_3} \text{ or } \frac{\partial \log f_3}{\partial n_2}$$

In the case of mixtures of strong electrolytes and weak electrolytes, electrolytes and non-electrolytes, etc., the various formulas of the present paper will depend on the choice of the thermodynamic "description": complete dissociation, incomplete dissociation, no dissociation.

Let us, for instance, consider a solution containing besides the solvent, λ_+ positive ionic species and λ_- negative ionic species obtained by dissolving a certain number of strong electrolytes. We first try to determine the minimum number of neutral components in terms of which the properties of the solution can be studied. Activity coefficients which are thermodynamically significant are average ionic coefficients of neutral components:

$$f_\pm = (f_+^{\nu_+} \cdot f_-^{\nu_-})^{1/\nu} \tag{35}$$

f_+ and f_- are the activity coefficients of the positive and of the negative ions. v_+, v_- are the numbers of positive and negative ions in the neutral component ($v = v_+ + v_-$). If z_+ and z_- are the algebraic values of the valences we have:

$$v_+z_+ + v_-z_- = 0 \tag{36}$$

The number of neutral components necessary to describe the properties of the solution is at most $\lambda - 1$ (in which $\lambda = \lambda_+ + \lambda_-$) (3) and at least λ_+ or λ_- (λ_+ if $\lambda_+ > \lambda_-$, λ_- if $\lambda_- > \lambda_+$). The neutral components having been chosen, the thermodynamic reasoning developed in this paper applies to the activity coefficients $f_{\pm,i}^{v_i}$. For instance, the reciprocity relations 9 become:

$$\frac{\partial \log f_{\pm,i}^{v_i}}{\partial n_j} = \frac{\partial \log f_{\pm,j}^{v_j}}{\partial n_i} \tag{37}$$

The activity coefficients appearing in 7 and 8 are replaced by $f_{\pm,i}^{v_i}$, $f_{\pm,j}^{v_j}$, etc.

SUMMARY

It is shown that, at given temperature and pressure, the various activity coefficients of a solution consisting of the solvent and of $x - 1$ solute species satisfy x differential equations of the Gibbs-Duhem type and $\frac{x(x-1)}{2}$ reciprocity relations of the type:

$$\frac{\partial \log f_i}{\partial n_j} = \frac{\partial \log f_j}{\partial n_i}.$$

The knowledge of

$$x^2 - \left[x + \frac{x(x-1)}{2}\right] = \frac{x(x-1)}{2}$$

non-thermodynamic relations between the various $\frac{\partial \log f_i}{\partial n_j}$ and the n_i's is thus required in order to obtain the total differentials of all the $\log f_i$'s, which are then calculated by means of quadratures, supplemented by the assumption that $f_i = 1$ at infinite dilution. After a discussion of certain special forms of the Gibbs-Duhem formulas the correct generalized form of the Duhem-Margules formula is obtained. The introduction of average ionic activity coefficients in the Gibbs-Duhem formula is discussed.

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THE DETERMINATION OF THE DEGREE OF PURITY OF LIQUID SUBSTANCES AND AZEOTROPIC MIXTURES

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During the last few years (1) the differential ebullioscopic apparatus has been so improved that it now seems possible to propose a standardized type of apparatus and to state the conditions for carrying out the determination of the degree of purity of either single liquid substances or of azeotropic mixtures.

Figure 1 represents the standardized type of ebullioscope for such purposes. This apparatus differs from the former one in that it has two drop-counters, f_1 and f_2, instead of one. To the drop-counter f_2 is sealed a reflux tube by means of which the liquid can be heated with either a small micro-burner, l, or an electric heater. This device enables one to collect a certain quantity of relatively volatile impurities in the upper part of the apparatus and thereby to increase the difference between the boiling point, t_1, measured in the lower part of the ebullioscope, and the temperature of condensation, t_2, measured in the upper part. The two drop-counters enable one to fix the intensity of the heating and to standardize the conditions of the experiment.

The degree of purity of a single liquid substance or of an azeotropic mixture is characterized by the difference $\Delta t = t_1 - t_2$ between the two above-mentioned temperatures. It is evident that, in the case of an absolutely pure single substance or of an ideal azeotropic mixture, this difference Δt is practically zero, because the correction for the difference of pressures at the levels t_1 and t_2, where the temperatures are measured, does not exceed 0.001°C. But since every liquid, even the most highly purified one, contains impurities, certain differences of $\Delta t > 0$ are noted, which depend on the nature and the amounts of the impurities. Since the difference Δt depends upon the degree of dephlegmation of the vapors present in the whole apparatus, the intensity of the heating should remain constant throughout. This condition may be fulfilled by adjusting the rate of flow through the two drop-counters measured by the numbers n_1 and n_2 of drops falling from the latter per unit time for a given intensity of heating; the number of drops depends upon the heat of vaporization and upon the boiling point of the liquid. Our experiments with water have led us to fix

for n_1 a value of 40 drops per minute. For other liquids which boil at $t_1 < 100°C.$ the following empirical relation can be used:

$$n_1 = \frac{900}{d \cdot L}$$

where L represents the molecular heat of evaporation expressed in kilogram-calories, and d the density of the liquid. When $t_1 > 100°C.$ the number of drops should be correspondingly greater. Good results can be obtained

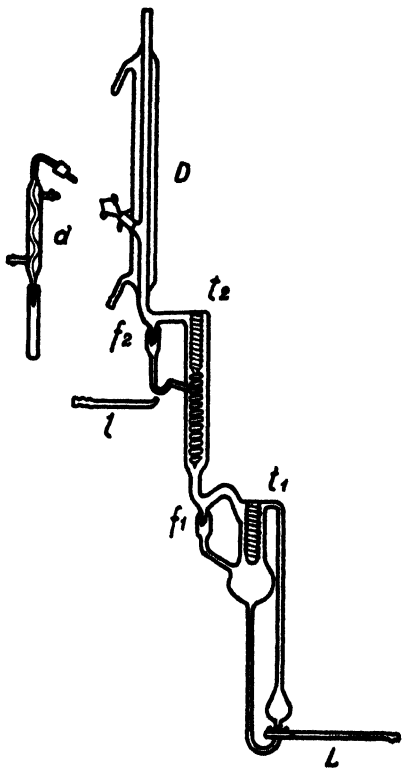

FIG. 1. THE EBULLIOSCOPE

with $n_2 = 0.9\, n_1$, or $n_1 = n_2$. The size of the flame of the microburner, l, should be regulated so that this relation can be obeyed.

For the estimation of the degree of purity of liquid substances the following measurements should be carried out: (1) the determination of the boiling point and the temperature of condensation of the substance under atmospheric pressure and the comparison of both points with the boiling point of water as the primary standard substance, or of another substance chosen as secondary standard; (2) the determination of the same temperatures after removal by distillation of a small quantity of the liquid.

This last operation seems to be necessary in almost all cases. Indeed, it often happens that very pure liquids contain minute traces of moisture or other impurities which can easily be removed by evaporating several cubic centimeters of the liquid (4). For this purpose the water is removed from the reflux condenser D, the small condenser, d, is joined to the tube provided with a ground joint, and a gradual distillation of 2 cc., 2 cc., and 2 cc. of the liquid is performed. After each distillation the difference Δt is measured. In this way it can be found whether the moisture present in the liquid or introduced as vapor adsorbed by the internal surface of the ebullioscope can be removed by this simple operation.

The investigation should be carried out as follows: (1) Before use the walls of the apparatus should be thermally isolated. Tube 1 should be wrapped with wet asbestos strips; after they are dry they fit closely to the surface of the Pyrex glass. The tubes in which the temperatures are measured are also wound with strips which are fastened round the tubes by means of thin copper wire. On top of the burner L an asbestos roof of conical shape is provided. (2) The ebullioscopic apparatus should be carefully dried and filled with a given amount of liquid under investigation (15 cc.). After allowing the liquid to boil for ten to fifteen minutes the apparatus is emptied, then refilled with a new portion of the same liquid; the same process is repeated, the liquid being once more poured out. Finally the apparatus is filled with 50 cc. of the liquid to be actually measured. (3) The temperatures should be determined with the accuracy of $\pm 0.001°C$. For this purpose the electrical resistance thermometer or the Beckmann mercury thermometer (modified by me) or that of Roberteau, etc., may be used. When Roberteau's thermometer is selected, the enlargement between the scale and the bulb called "grain" must be immersed in mercury. Each thermometer should be immersed to the same extent in both tubes, t_1 and t_2. (4) The intensity of the heating with both burners should be regulated as already stated. (5) The determination of the two above-mentioned temperatures should be carried out by using the same thermometer. For this purpose the method of successive measurements should be applied (an example of this method is given in table 1). The boiling point of water or other substance chosen as the standard liquid (2, 5) is measured simultaneously. If another substance than water is used as standard, its boiling point should differ only slightly from the boiling point of the liquid under examination, so that its boiling point may be measured by transferring the same thermometer from one ebullioscope to another. (6) After having determined the difference Δt (first difference) the small condenser d is joined to the side-tube of the condenser D and the water is removed from this condenser. Afterwards three 2-cc. portions of the liquid are carried over into the small test tube by successive distillation. After each distillation the determination of the difference Δt is carried out. If all the successive differences, Δt, Δt_1, Δt_2, Δt_3, or at least the last two remain

practically constant, $\Delta t > \Delta t_1 = \Delta t_2 = \Delta t_3$ or $\Delta t > \Delta t_1 > \Delta t_2 = \Delta t_3$, the value Δt_2 may be accepted as a basis for characterizing the degree of purity of the investigated liquid. If, however, the above-mentioned differences gradually decrease, $\Delta t > \Delta t_1 > \Delta t_2 > \Delta t_3$, it proves that the impurity cannot be removed by this operation and that consequently the second difference, Δt_1 ought to be accepted as the characteristic value for the degree of purity of the sample investigated. In both cases all the successive differences, Δt, Δt_1, Δt_2, Δt_3, should be stated in order to give some idea as to the nature

TABLE 1

Determination of the purity of isopropyl alcohol

TIME	t_1	t_2*	Δt	t_{Bar}	ΔT
11.00	4.978			2.430	
11.02	4.979			2.430	
11.04	4.979			2.429	
				2.430	
				2.430	
11.10	(4.979)	4.783	0.196	2.430	
11.12	(4.979)	4 786	0 193	2 430	
11.14	(4.979)	4.780	0.199	2.430	
First difference....			0 196		
11.18	4.979				
11.20	4 979				
11.22	4 979				
11.28	(4.979)			3.013	1.966
11.30	(4.979)			3.013	1.966
11.34	(4 979)			3.013	1.966
11.36					
11.38					
11.40	4.979				
11.42	4.979				
11.44	4.979				

* The condensation temperature varies between relatively large limits on account of the presence of a large amount of volatile impurities.

of the impurities present in the liquid under examination. For the present it appears that actually the following scale may be accepted for characterizing the degree of purity of liquid substances:

Degree of purity	*Limits in degrees for the difference Δt*
First degree of purity (I)	1.00 to 0.10
Second degree of purity (II)	0.10 to 0.05
Third degree of purity (III)	0.05 to 0.02
Fourth degree of purity (IV)	0.020 to 0.005
Fifth degree of purity (V)	0.005 to 0.000

If the liquid is, however, characterized by the fifth degree of purity, a more careful investigation ought to be carried out with the help of a more sensitive differential ebullioscope.

At the present time the differential ebullioscope with several sections (3) seems to be the most convenient for this purpose.

The degree of purity of isopropyl alcohol (Schering-Kahlbaum) was determined by means of a standardized ebullioscope (table 1). Benzene, selected as a secondary standard, has a boiling point $t_{Bar} = 80.122°C.$ at 1 atmosphere. The first difference, Δt, between the boiling point and the condensation temperature was determined. The difference between the boiling points of the two liquids examined is equal to $\Delta t = 1.966$. After the introduction of the correction for the true value of the degree, the difference, $t_{Bar} - t_1 = \Delta T$, becomes equal to 2.060, therefore the boiling point of isopropyl alcohol, t_a, equals 82.18°C. By successive distillation of three 2-cc. portions of the liquid, the following results have been obtained:

$\Delta t_1 = 0.195$	$\Delta T_1 = 2.098$	$t_a' = 82.22$
$\Delta t_2 = 0.144$	$\Delta T_2 = 2.108$	$t_a'' = 82.23$
$\Delta t_3 = 0.083$	$\Delta T_3 = 2\ 124$	$t_a''' = 82\ 25$

CONCLUSIONS

Control of the purity for the given sample of isopropyl alcohol proves that the impurities cannot be removed by distillation of a small quantity of the liquid. In accordance with the scale proposed above, the degree of purity seems characterized by the first difference, $\Delta t = 0.195$. The boiling point of the liquid, t_a, is equal to 82.22°C. at 1 atmosphere, which is 2.10° higher than the boiling point at 1 atmosphere of benzene, the secondary standard substance. After distillation by help of a rectification column with twenty-one bulbs the determination of the degree of purity of the purified isopropyl alcohol has been carried out. The following result has been obtained: $\Delta t = 0.010$; $\Delta t_1 = 0.009$; $\Delta t_2 = 0.009$; $\Delta t_3 = 0.008$; $\Delta T_3 = 2.17$; $t_a''' = 82.29°$ ($p = 1$ atmosphere).

It follows that in accordance with our scale, the sample of the purified isopropyl alcohol can be considered as having the IV-th degree of purity, Δt being equal to 0.009°, and the boiling point to 82.29°. The boiling point of the investigated isopropyl alcohol is 2.17° higher than the boiling point of benzene, the secondary standard substance ($p = 1$ atmosphere).

SUMMARY

The application of a standardized differential ebullioscope for determining the degree of purity of single liquid substances and azeotropic mixtures has been described. Brief instructions are given for executing the investigation. A scale for characterizing the relative degree of purity of liquid substances and azeotropic mixtures has been proposed.

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X-RAY STUDIES ON THE HYDROUS OXIDES. VI

ALUMINA HYDRATES

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Two years ago (19) it was concluded, as a result of x-ray and dehydration studies, that only two hydrates of alumina exist: γ-$Al_2O_3 \cdot 3H_2O$ (gibbsite) and α-$Al_2O_3 \cdot H_2O$ (diaspore). No indication was found for the existence of a second trihydrate, α-$Al_2O_3 \cdot 3H_2O$ (Fricke's bayerite), or of a second monohydrate, γ-$Al_2O_3 \cdot H_2O$ (böhmite). From the available evidence, it was believed that precipitated alumina was hydrous "δ-Al_2O_3" rather than hydrous γ-$Al_2O_3 \cdot H_2O$. In the light of recent developments it now appears that certain of these conclusions must be modified and extended.

α-ALUMINA TRIHYDRATE

While our first paper was in the process of publication, an article by Fricke and Severin (7) appeared in which definite evidence was presented to prove that α-$Al_2O_3 \cdot 3H_2O$ (bayerite), isomeric with gibbsite, exists. The α-$Al_2O_3 \cdot 3H_2O$ gives a distinctive x-ray diffraction pattern and a dehydration isobar characteristic of a trihydrate. Synthetic γ-$Al_2O_3 \cdot 3H_2O$ is formed by the slow hydrolysis of aluminates (Bonsdorff and Goudriaan). On the other hand, if the separation takes place relatively quickly, the metastable isomer, α-$Al_2O_3 \cdot 3H_2O$, is first formed and goes over spontaneously into γ-$Al_2O_3 \cdot 3H_2O$ in the course of a few weeks in contact with dilute alkali. We failed to observe the formation of α-$Al_2O_3 \cdot 3H_2O$ either by the method of Goudriaan or that of Bonsdorff, since the precipitate remained in contact with the alkali for 30 days before it was subjected to x-ray analysis and was therefore largely γ-$Al_2O_3 \cdot 3H_2O$.

A pure sample of α-$Al_2O_3 \cdot 3H_2O$ sent us by R. P. Rooksby has been examined by the x-ray diffraction method. Comparison of the x-ray diagram of α-$Al_2O_3 \cdot 3H_2O$ shows that some of our samples, previously considered to be mixtures of γ-$Al_2O_3 \cdot 3H_2O$ and δ-Al_2O_3, contained considerable amounts of α-$Al_2O_3 \cdot 3H_2O$. For example, diagrams 3, 4, and 6 of figure 3 and 1 to 5 and 8 of figure 6 (20) are for samples that we now know to be largely α-$Al_2O_3 \cdot 3H_2O$.

γ-$Al_2O_3 \cdot H_2O$ VERSUS "δ-Al_2O_3"

More than twelve years ago L. H. Milligan (16) dehydrated a sample of artificial gibbsite in a current of air containing a known amount of water vapor. The dehydration isobar showed conclusively that the sample was a trihydrate, but it gave no indication whatsoever of the formation of a monohydrate. Since both Rooksby (17) and ourselves have obtained a material that gives the same x-ray diffraction pattern as γ-$Al_2O_3 \cdot H_2O$ (böhmite) by the thermal dehydration of α-$Al_2O_3 \cdot 3H_2O$ (gibbsite), it is important to explain, if possible, why the isobars fail to reveal the presence of a monohydrate.

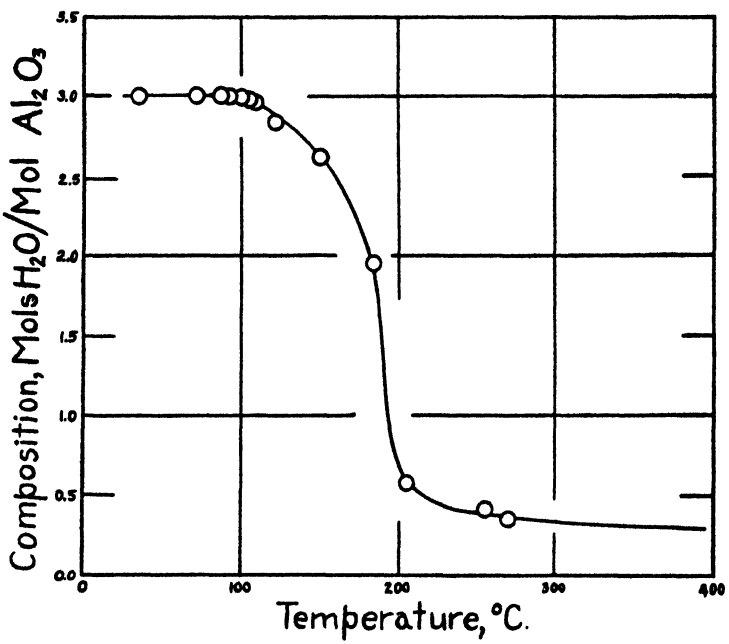


FIG. 1. DEHYDRATION ISOBAR OF γ-$Al_2O_3 \cdot 3H_2O$ (SYNTHETIC GIBBSITE)

Dehydration isobar of artificial gibbsite

A sample of γ-$Al_2O_3 \cdot 3H_2O$ was dehydrated in an apparatus similar to that of L. H. Milligan previously described (20). Special care was taken to secure equilibrium values. It was found that many days were required at the lower temperatures and many hours at the higher temperatures. The results are shown graphically in figure 1. It is apparent that the isobar gives no evidence whatsoever of the formation of monohydrate. X-ray analyses of samples taken at intervals from a second container give the results shown in table 1.

A dehydration isobar almost identical with figure 1 was obtained with gibbsite by Fricke and Severin (7). They also made the isobars for the

α-trihydrate or bayerite and for both α-$Al_2O_3 \cdot H_2O$ (diaspore) and γ-$Al_2O_3 \cdot H_2O$ (böhmite). These curves, reproduced in figure 2, are noteworthy since extreme care was taken to ensure equilibrium. In some cases several weeks were required to get a single point, and the value recorded was taken only after the system remained in equilibrium for from eight to twenty-five days.

TABLE 1

X-ray diffraction data obtained during the dehydration of artificial gibbsite

TEMPERATURE	TYPE OF PATTERN
degrees C.	
35–150	γ-$Al_2O_3 \cdot 3H_2O$ (gibbsite)
185	γ-$Al_2O_3 \cdot H_2O$ (böhmite) and γ-$Al_2O_3 \cdot 3H_2O$
205–410	γ-$Al_2O_3 \cdot H_2O$

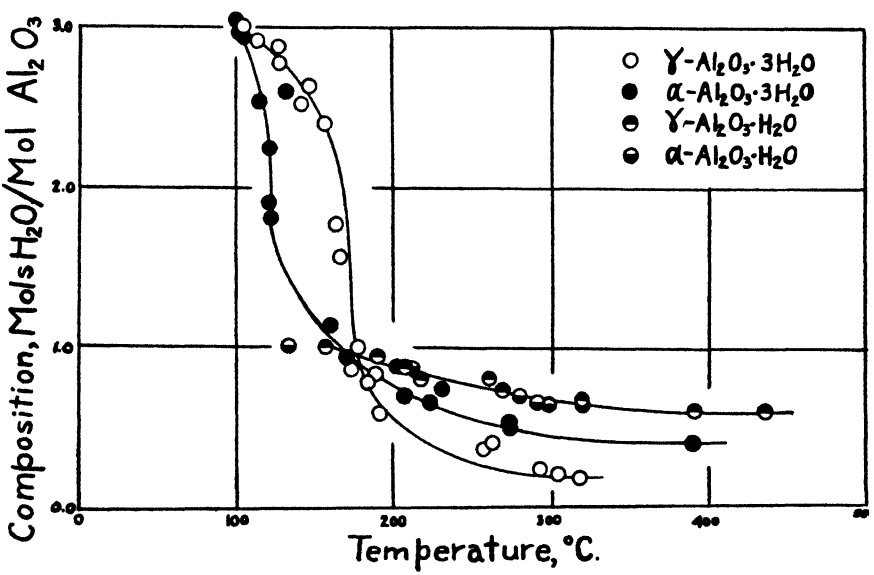


FIG. 2. DEHYDRATION ISOBAR OF α- AND γ-$Al_2O_3 \cdot 3H_2O$ AND α- AND γ-$Al_2O_3 \cdot H_2O$

After Fricke and Severin

In the light of the above work there can be no question about the facts. The monohydrate formed by the decomposition of γ-$Al_2O_3 \cdot 3H_2O$ does not undergo decomposition at a definite temperature as a real hydrate usually does. Indeed in the experiment shown in figure 1, a sample at 410°C., having a composition of approximately $Al_2O_3 \cdot 0.34H_2O$, gave the x-radio-

gram of γ-$Al_2O_3 \cdot H_2O$ only. This would be impossible if the hydrate were behaving in a normal way. Furthermore, Fricke and Severin's curve for the monohydrate is a typical desorption curve showing no indication whatsoever of a break. It is this sort of evidence which formerly led us to conclude that the alleged monohydrate was not a true hydrate but an alumina with adsorbed water.

The only evidence advanced by Rooksby (17) in support of the view that the initial product of the thermal dehydration of γ-$Al_2O_3 \cdot 3H_2O$ is a monohydrate, was an analysis of the product. But the dehydration curves of L. H. Milligan, Fricke and Severin, and ourselves show that this composition was accidental and could not possibly have been an equilibrium value. More recently Edwards and Tosterud (6) claimed that the compound formed by heating precipitated alumina under pressure, analyzed for a monohydrate, gave the γ-$Al_2O_3 \cdot H_2O$ x-ray pattern, and exhibited a thermal arrest in the heating curve. The first two lines of evidence will not definitely distinguish between a monohydrate and a hydrous alumina with the right amount of adsorbed water, and an arrest in the heating curve of an oxide–water system does not necessarily indicate the presence of a true hydrate (10). In this case the arrest might be offered as evidence of a polymorphic change from "δ-Al_2O_3" to γ-Al_2O_3. However, preparations which give the γ-$Al_2O_3 \cdot H_2O$ (böhmite) pattern can be obtained in well-defined macroscopic crystals which analyze for monohydrate. Thus Fricke and Severin (7) obtained it by heating commercial alumina trihydrate to 350–370°C. at a pressure of 200 atmospheres. Hüttig and Peter (11) prepared a similar product by heating the trihydrate in a bomb tube at 200 atmospheres. Particularly good crystals were formed by heating 4–20 per cent aluminum nitrate containing up to 20 per cent of nitric acid at 320–360°C. and 200 to 300 atmospheres (12, 13). In the light of this positive evidence there can no longer be any doubt that böhmite is γ-$Al_2O_3 \cdot H_2O$. But having reached this conclusion one is obliged to explain the absence of any sign of a break corresponding to the monohydrate in the dehydration isobars of γ-$Al_2O_3 \cdot 3H_2O$ and γ-$Al_2O_3 \cdot H_2O$.

Interpretation of the dehydration isobars

Application of the phase rule to the two-component system hydrate–oxide–water vapor, shows that the system should be univariant. The type of isobar is given by the dotted lines in figure 3. Theoretically, the curve should drop to zero composition at a definite temperature, but actually the isobars are usually rounded off, as shown in the figure by the broken line *ADC*. This is due to a loss of part of the water below the true decomposition temperature of the mass of the hydrate on account of lattice distortion, strain in the crystals, and variation in crystal size. Now if the oxide formed by the dehydration of the hydrate is highly hygroscopic, it

will adsorb most of the water vapor. Hence the actual dehydration measured is the loss of adsorbed water from the oxide. In such cases a bivariant type of curve is to be expected, as shown by the solid line *AE* in figure 3. It is precisely this last type of curve which Fricke and Severin obtained for both α- and γ-$Al_2O_3 \cdot H_2O$.

We can now explain the persistence of the x-radiogram of the monohydrate where it would ordinarily not be expected to exist. The x-radiogram for the monohydrate should persist along the broken curve *ADC*, because some monohydrate exists as such, and the very highly hygroscopic γ-Al_2O_3 (1, 2, 4, 5, 15, 18, 21), formed by partial decomposition of the former, is either amorphous or too finely crystalline to be detected by x-ray analysis.

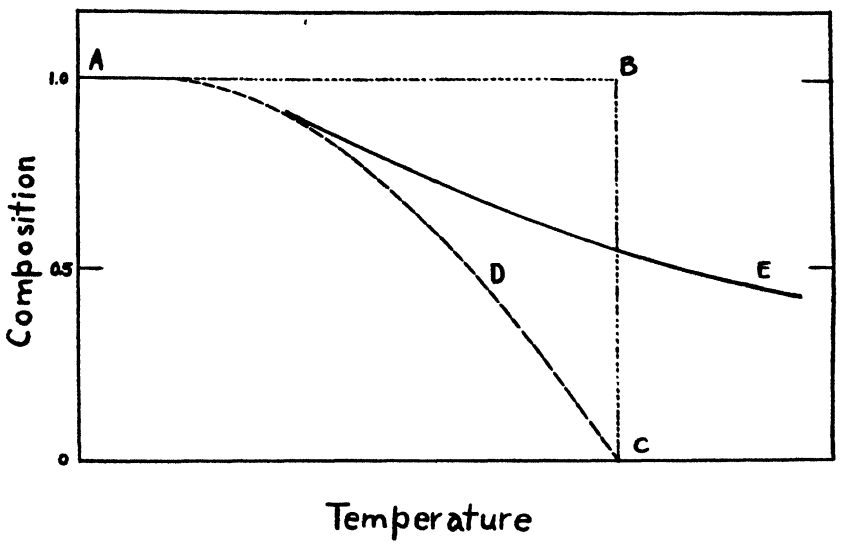


FIG. 3. ISOBARIC EQUILIBRIUM IN THE SYSTEM HYDRATE–OXIDE–WATER VAPOR

In the case of a higher hydrate decomposing first into a lower hydrate and finally into the anhydrous substance, it is apparent that under the conditions noted above, the isobar will fail completely to detect the lower hydrate. In figure 4 the theoretical curves for the case of a trihydrate decomposing to a monohydrate and this in turn to the oxide are given by the dotted lines. The actual experimental curve is given by the solid line. The composition of the trihydrate remains constant until at point *F* some water is lost, giving a small amount of water vapor and monohydrate. As this process continues along *FK* and along *KH* all the trihydrate decomposes rapidly, giving monohydrate. Now at this temperature the lower hydrate loses water to point *O* and hence the line *FKH* continues past the theoretical composition of the monohydrate to the point *O*. This decom-

position of the monohydrate gives the highly adsorptive γ-oxide, the presence of which causes the dehydration to proceed along the line *HOE* for the reason given above.

Although the case under consideration is unusual it is not unique. Thus a curve somewhat similar to the one shown in figure 4 is obtained for the dehydration of gypsum, which yields plaster of Paris as an intermediate product (3, 4, 8, 9, 14). The latter compound is said to be $CaSO_4 \cdot 0.5H_2O$, but this would not follow from the dehydration curve, which is like *KHE* in figure 4 rather than like *GHB*. Here again, the

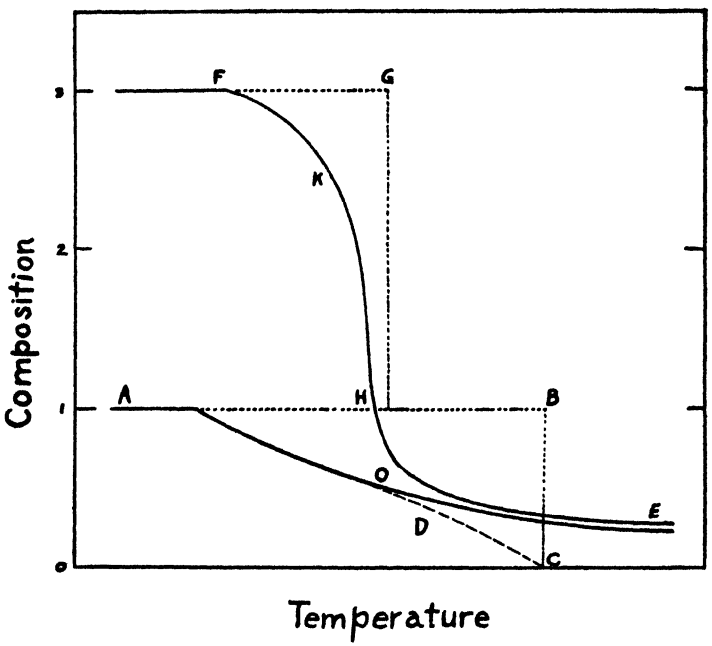


FIG. 4. ISOBARIC EQUILIBRIUM IN THE SYSTEM HYDRATE–LOWER HYDRATE–WATER VAPOR

highly hygroscopic character of the anhydrite resulting from the decomposition of hemihydrate adsorbs a part of the water, and the dehydration of this hydrous material determines the form of the curve.

SUMMARY

The following is a brief summary of the results of this investigation:

1. Slow hydrolysis of an aluminate solution gives a definite metastable alumina hydrate, α-$Al_2O_3 \cdot 3H_2O$ (bayerite), different from γ-$Al_2O_3 \cdot 3H_2O$ (gibbsite). Aging of this metastable hydrate, especially in contact with alkali, gives γ-$Al_2O_3 \cdot 3H_2O$. The present authors overlooked the labile modification since they allowed the products made by the method of Goud-

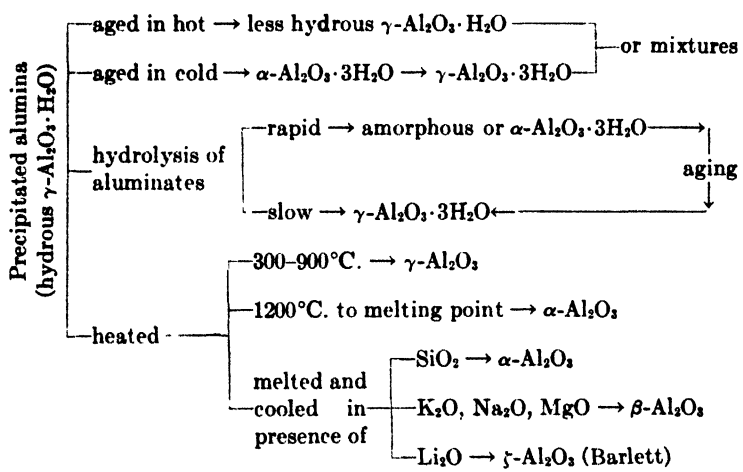
riaan and Bonsdorff to stand in contact with alkali for 30 days. That α-$Al_2O_3 \cdot 3H_2O$ is a definite hydrate has been conclusively proven by dehydration isobars obtained recently by Fricke and Severin.

2. Dehydration isobars of γ-$Al_2O_3 \cdot 3H_2O$ made by L. H. Milligan over twelve years ago, and by Fricke and Severin, and by the present authors more recently, show no indication whatsoever of the formation of a monohydrate. However x-ray examination of the intermediate dehydration product gives the pattern attributed to γ-$Al_2O_3 \cdot H_2O$ (böhmite). This is the same material that the present authors formerly considered to be hydrous "δ-Al_2O_3" because of the form of the dehydration curve.

3. Well-defined macroscopic crystals of γ-$Al_2O_3 \cdot H_2O$ have been made (Fricke and Severin, Hüttig and Peters, Ipatiew), but the dehydration isobar of the compound is a typical desorption curve.

4. In this paper an explanation is suggested for the apparently anomalous behavior of the dehydration isobars of both γ-$Al_2O_3 \cdot 3H_2O$ and γ-$Al_2O_3 \cdot H_2O$, based on the fact that the thermal decomposition of the latter gives a very highly adsorptive oxide (γ-Al_2O_3) which adsorbs most of the water vapor. Dehydration of this hydrous oxide gives a bivariant curve.

5. The various transformations of precipitated alumina may be tabulated in the following diagram, which is a revision of the diagram given in Part I of this series of papers:



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THE CONSTANCY OF THE URANIUM-ACTINIUM RATIO IN MINERALS[1]

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The status of the actinium series has always been a subject of conflicting experimental findings and of interpretations leading to controversies. Boltwood (1), in 1908, showed that the actinium series was associated with uranium and not with thorium. The determination of the fraction of the uranium atoms disintegrating to form the actinium series, earlier called the "branching ratio" and later called the "activity ratio," has been accomplished by three distinct methods: First, by the determination of the relation between the alpha activity of thin films of protoactinium and pure uranium oxide; second, by the determination of the relation between the alpha activity of thin films of actinium and uranium oxide; third, by the determination of the relation by the comparison of the active deposits from actinon.

Numerical ratios from the first two methods are abundant in the literature: Boltwood (1), 1908, 4 per cent; Fussler (2), 1917, 2.2 to 3.3 per cent; Hahn and Meitner (4), 1919, 3 per cent; Meyer (5), 1920, 4 per cent; Widdowson and Russell (8), 1923, 2.9 per cent; Piccard and Kessler (7), 1924, 5 per cent; Wildish (9), 1930, 1.5 to 5.16 per cent; Gleditsch and Foyn (3), 1932, 2.7 per cent; A. von Grosse (11), 1932, 4 per cent. Meyer and Hess (6) were the only ones to use the active deposit of actinon to show the ratio constant.

A. von Grosse in determining the ratio as a constant, 4 per cent, used five minerals, one of which was the carnotite used by Wildish to find his 5.16 per cent ratio. von Grosse claims that zirconium is a better reagent than tantalum for the adsorption of protoactinium, which Wildish and others regard as the nearest analogue of protoactinium. Having on hand two minerals used by von Grosse and four of those used by Wildish, we undertook to determine the constancy of the ratio by a method independent of the chemistry of protoactinium, namely the method of Meyer and Hess (6). This method, however, does not give the percentage ratio, but does supply evidence as to the constancy of the ratio.

[1] This paper was read at the Midwestern Regional Meeting of the American Chemical Society held at Kansas City, Missouri, May 4, 1934.

METHOD

The method of Meyer and Hess (6), for the determination of the relative amounts of actinium in ore solutions by means of the active deposit of actinon, was modified for our experiments. Their method consisted of passing air through a solution of the mineral contained in a liter flask and into a rectangular brass box, which contained an insulated brass plate, 2 × 12 cm. The brass plate was 1 cm. from the bottom of the brass box, the inner dimensions of which were 4 × 15 × 3 cm., and was charged negatively to a potential of 460 volts. The air was allowed to flow through the apparatus at a known rate for 1 hour. The activity of the plate was determined by measuring it in a condenser connected to a Wulf string

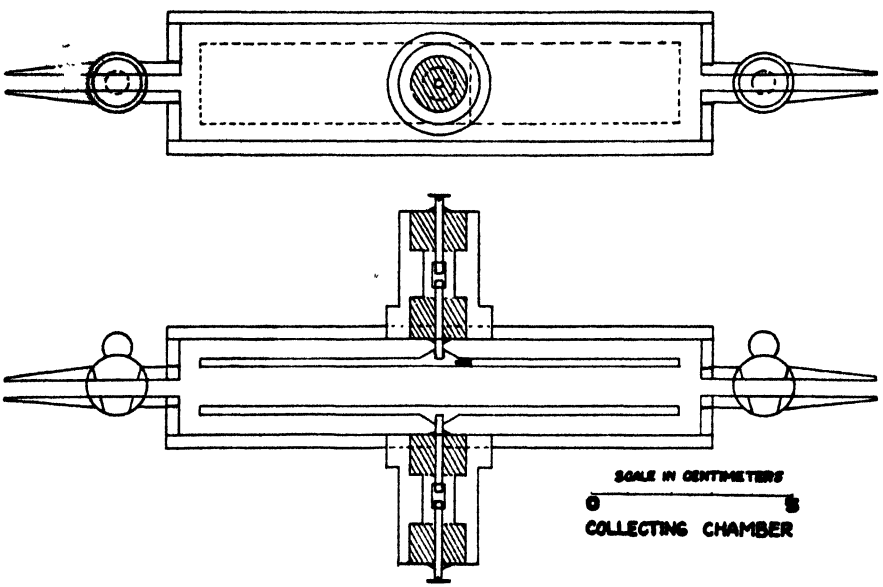

FIG. 1. COLLECTING CHAMBER

electrometer. The success of the method depends upon the maintenance of a reproducible rate and time of air flow through the apparatus.

For our experiments the method was modified so that, using the same flow of air and the same potential on the collecting plates, the apparatus allowed the simultaneous deposition of the active deposit from the actinon continually produced in the solution of two different minerals, thereby eliminating effects due to fluctuations in the rate of flow of the air. The collecting chambers differed from those used by Hess and Meyer; two insulated brass plates were placed 1 cm. apart in a rectangular brass box with inner dimensions 3 × 13 × 2 cm. (figure 1). The upper plate of each chamber was maintained at a negative potential of 500 volts; the lower

plate was connected through the ground to the positive side of the source. The upper plate was removable. Two similar, Drechsel type, gas-washing cylinders, of 600-cc. capacity and equipped with spray bubblers, held the solutions under test.

A stream of air is forced through an air meter, through the first solution, through a glass wool plug and drying tube, and thence into the first collecting chamber. From this chamber, the air passes into a 7-liter carboy, where the actinon remaining in the air decays completely, and thence through the second solution and collecting chamber. This air stream removes the actinon from the solution of the ore, where it is being formed continually, and carries it into the chamber in which the actinon decays to produce actinium A. This immediately decays to produce positive ions of actinium B, which are deposited in the electric field on the negatively charged upper plate.

Before a run was started, the air was allowed to pass through the solutions and around the chambers through an alternate path; this procedure removed any radon that might have accumulated in the solutions. The air was then shunted into the chambers by manipulating the stopcocks, and the upper plates charged by a small generator. The runs were all of one hour duration, for which time the air flow was between 120 to 180 liters.

The upper plates were then removed and their activities determined alternatively in a Wulf (10) bifilar, quartz fiber electroscope. In order for the plates to be placed inside of the ionization chamber of the electroscope, they were constructed in two sections, mortised together (figure 1). This joint was broken and each section set in place in a specially constructed glass rack, which fitted rigidly into the ionization chamber of the electroscope. Four values of the activity of each plate were determined for accurate time intervals after the conclusion of the deposition.

Although the time taken in reading the electroscopic drift was from 0.5 to 5 minutes, the decay of actinium B is so rapid that only the average activity is gotten for that time interval. In order to obtain the instantaneous activity for the time at which reading is begun, the following formula must be applied: $A = \bar{A}t/(1 - e^{-\lambda t})$, where A is the instantaneous activity, $\bar{A}$ is the average activity which is obtained from reading the electroscope, t is the time interval of the reading, and λ is the decay constant of actinium B.

After these four values of instantaneous activity for each deposit have been calculated, they are extrapolated back to zero time by means of the formula: $A_0 = Ae^{\lambda t}$, where A_0 is the activity at the conclusion of the deposition, A the instantaneous activity at the time t, t the time elapsed between the conclusion of the deposition and start of the reading of the electroscope, and λ the decay constant of actinium B. These four values

for the activity of each deposit were averaged, and the ratio of the actinium in the two solutions under test was obtained. Four such runs were made for each solution of mineral, giving a ratio which was the mean of four means, or which depended upon sixteen individual readings. The ratio of the uranium in the two solutions was obtained from results of gravimetric analysis of the minerals.

Special care was taken to make the volume of air between the solution and the collecting chamber as nearly equal as possible for the two sections of the apparatus. Before the apparatus was used for the determinations, it was tested by determining the activity relation between the halves of a solution prepared by dissolving 200 g. of carnotite ore. The activity of the deposits from these two halves checked closely. Two gas meters were used, one at the source of the air stream and the other at the exit. Checking values were obtained for the amount of air entering and leaving the apparatus.

MATERIALS AND RESULTS

Two carnotites, three pitchblendes, one soddite and one thorianite, four of which were from the same samples used by Wildish (9) and two of which were from the same samples used by A. von Grosse (11), were used for the minerals whose relative actinium–uranium ratios were determined by our experiments.

One method applied to all of these minerals to get them into solution. In each case the mineral was digested in hot concentrated hydrochloric acid–nitric acid for forty-eight hours. The residue was then filtered from the solution, and fused with sodium carbonate containing a small amount of barium chloride. After leaching the fused mass with water, the carbonate residue was filtered off, taken into solution with hydrochloric acid and added to the original solution. If a residue remained after the hydrochloric acid treatment of the carbonate residue, it was again fused, etc. The filtrates from the leach solutions showed an absence of actinon when tested by subjecting them to a run similar to that used with the ore solutions.

Of these seven minerals, only two contained thorium in sufficient quantities to require correction for the activity of thorium B, which was deposited simultaneously with the actinium B. Actinium B decays to a negligible value in 3 hours, while thorium B requires several days. The activity of thorium B can be gotten 5 hours after its deposition, free from the activity of actinium B, and can be extrapolated back to the times of reading the activities of the mixture. In this way the values of the activities of the actinium B can be obtained for the minerals containing thorium. The smallness of the chambers and the high rate of air flow allowed for the activities of actinium B and thorium B to be present in about equal amounts at the time of the readings.

Since solution III, soddite, was used in the first solution cylinder throughout the course of our experiments, and the activities of the other solutions were compared with it, we arbitrarily referred to it as having an actinium–uranium ratio of unity. However, since solution V, G. B. L. pitchblende, was a portion of a sample whose uranium content had been determined very accurately, the ratios were converted so as to refer to it as having an actinium–uranium ratio of unity.

Table 1 summarizes the results of our experiment.

TABLE 1

Actinium–uranium ratio in minerals

Experimental values

MINERALS	SOLUTION NO	PER CENT OF URANIUM ELEMENT	URANIUM IN SOLUTION	RATIO U/U_{III}	RATIO Ac/Ac_{III}	RATIO Ac/U III AS UNIT RATIO	RATIO Ac/U V AS UNIT RATIO
			grams				
Carnotite*	I	30 6	30 6	0 873	0 661	0 753	0.809
Carnotite†	II	18 6	18 6	0 532	0.401	0.756	0 811
Soddite‡	III	43 8	35 0	1 000	1 000	1.000	1 072
Pitchblende, Bohemian§	IV	62 4	27 2	0 777	0.725	0 931	0 998
Pitchblende, G. B. L.¶	V	60 6	30 3	0 864	0.804	0.933	1 000
Thorianite**	VI	26 7	26 7	0 763	0.688	0 902	0.967
Pitchblende, Wilberforce‡‡	VII	53 5	53 5	1 546	1.527	1.012	1.085

* Naturita, Colorado; analyzed at the University of Missouri.

† Colorado; Wildish, 1930 (ratio of 5.16).

‡ Belgian Congo; Wildish, 1930.

§ Bohemia; Wildish, 1930.

¶ Canada; analyzed at the University of Missouri.

** Ceylon; Wildish, 1930.

‡‡ Canada; G. P. Baxter, 1930, from the same lot used for the Wilberforce lead atomic weight determination.

DISCUSSION AND CONCLUSION

The carnotites, solutions I and II, gave values for the ratio distinctly lower than the other minerals. Carnotite is generally considered a secondary mineral, is not compact, and is susceptible to leaching processes. For these reasons, the carnotites were excluded from the discussion of the constancy of the actinium–uranium ratio.

The individual experimental values for the "ratio Ac/Ac_{III}" are obtained from sixteen readings. These readings had a maximum deviation from their mean not exceeding 5 per cent. Since the uranium was determined gravimetrically, the error would be negligible in comparison with this deviation. Therefore, for our experiments, we place 5 per cent as our probable error. However, for the five minerals other than the carnotites, the maxi-

mum deviation from the mean of the "ratio Ac/U" is slightly below 6 per cent. This falls slightly outside of the value set as experimental error.

The results of our experiments seem to justify the conclusion that the ratio of actinium to uranium for the minerals examined is a constant. And since our minerals are representative, we venture to add that the ratio is a constant for all unaltered minerals. However we must add that our method limits us to only a constant ratio and prohibits the assignment of any numerical values to this constant.

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THE KINETICS OF THE OXIDATION OF GASEOUS PROPIONALDEHYDE

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INTRODUCTION

Aldehydes are of considerable importance in the mechanism of the oxidation of most gaseous organic compounds. As a result a considerable amount of work has been done on the oxidation of gaseous acetaldehyde (1, 3, 4). The acetaldehyde oxidation, however, is complicated and the mechanism is by no means clear. It is therefore of interest to investigate the oxidation of other aliphatic aldehydes where some of these complications might be absent. The present paper deals with the kinetics of the oxidation of gaseous propionaldehyde.

EXPERIMENTAL

The reaction was investigated by introducing propionaldehyde and oxygen separately into a heated vessel and observing the rate of change of pressure as the reaction proceeded. The apparatus was similar to that used in a previous investigation (3). The required temperatures were obtained by means of an electric furnace, the reaction vessel, a 200-cc. Pyrex bulb, being packed into the furnace with coarse iron filings to ensure uniformity of temperature. The temperature was measured with a standardized mercury thermometer, and could be maintained constant to within 1°C.

Propionaldehyde from three sources was used, viz., Kahlbaum, Eastman Kodak, and Eimer and Amend. In each case it was purified by fractional distillation. The three samples gave identical results. Commercial oxygen was obtained from cylinders. It contained 6.4 per cent nitrogen, and was purified merely by drying with phosphorus pentoxide.

EXPERIMENTAL RESULTS

The reaction was investigated from 120°C. to 170°C. No appreciable effect due to the aging of the reaction vessel was noticed after the first ten or fifteen runs. It was also found that neither the degree of evacuation nor the temperature at which this was carried out had any appreciable effect on the succeeding run.

In all runs reported here, oxygen–aldehyde mixtures were made up by introducing the reactants separately into the reaction bulb. (The order of admission had no effect.) This was done because it was found that the maximum pressure decrease associated with the reaction was diminished about 15 per cent, and the rate of reaction was diminished by about 40 per cent, if the reactants were mixed outside the reaction bulb in the presence of a mercury manometer. Tests showed the presence of peroxides under these conditions.

The pressure change accompanying the reaction

As the reaction proceeded the pressure diminished. The maximum decrease amounted to about 73 per cent of the initial partial pressure of the

TABLE 1

Maximum pressure decrease

TEMPERATURE	OXYGEN–ALDEHYDE RATIO	INITIAL PARTIAL ALDEHYDE PRESSURE	MAXIMUM PRESSURE DECREASE
degrees C.		*cm.*	*per cent*
150.8	2.52	20.00	73
150.8	1.05	20.00	69
150.8	4.39	12.00	74
150.8	1.36	12.00	71
150.8	1.01	8.85	70
150.8	1.06	9.40	68
150.8	0.90	8.85	63
150.8	0.76	8.75	52
150.8	1.23	5.65	63
139.1	2.86	20.00	75
139.1	3.54	12.00	71
125.3	2.87	20.00	74
125.3	1.96	20.00	76

aldehyde. The pressure then slowly rose again. The maximum pressure decreases obtained in a number of typical cases are shown in table 1.

As shown in table 1, the maximum pressure decrease is constant and independent of the experimental conditions, provided that (a) the partial aldehyde pressure is not much below 8 cm., and (b) the oxygen–aldehyde ratio is not much below 1.00. In as much as the pressure decrease is followed by a pressure increase, it is evident that the reaction proceeds in stages. Since in most cases the maximum decrease is constant, however, there is no doubt that it is justifiable to use the rate of pressure change as a measure of the rate of reaction. In the cases where the full pressure decrease is not reached, it is probably justifiable to employ the same

criterion of reaction if we consider only the early part of the process. In consequence we have used the time for the pressure to change from a 15 per cent decrease to a 30 per cent decrease as a measure of the rate of reaction.

The rate of reaction

Complete data for some typical runs are given in table 2, and are plotted in figure 1. It will be seen that as is usual in gaseous oxidation reactions, there is a small induction period.

Table 3 gives values for $T_{30} - T_{15}$ under various conditions.

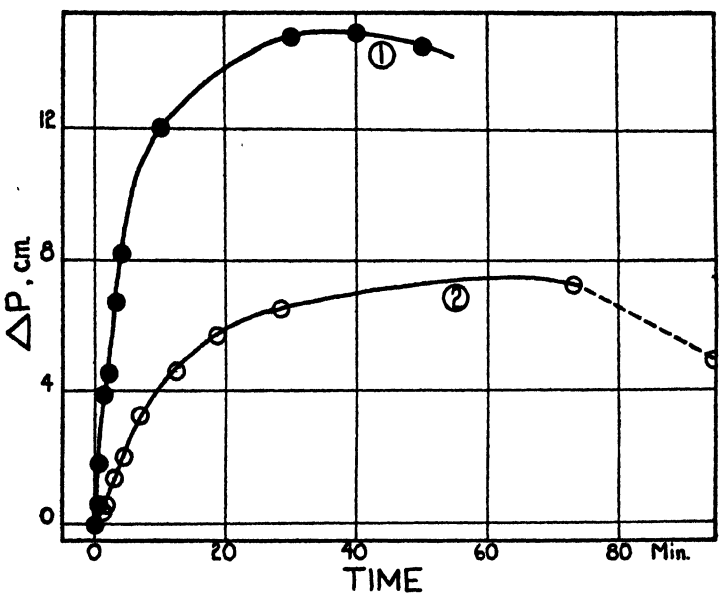

FIG. 1. TYPICAL PRESSURE–TIME CURVES

Temperature, 150.8°C. Curve 1: C_2H_5CHO, 20.0 cm.; O_2, 50.4 cm. Curve 2: C_2H_5CHO, 9.7 cm.; O_2, 38.8 cm.

The effect of pressure

For any given oxygen–aldehyde ratio, the effect of the total pressure on the rate corresponds to an order of about 2.0. The effect of the oxygen concentration on the rate of the reaction is shown by figure 2, in which $T_{30} - T_{15}$ is plotted against the oxygen–aldehyde ratio for various constant initial partial pressures of aldehyde. It will be seen that the rate is virtually independent of the oxygen concentration if the oxygen–aldehyde ratio is above 2.0. When the oxygen concentration is reduced below this value, the rate is somewhat diminished.

TABLE 2

Data for typical runs at 150.8°C.

$P_{ald.}$, 9.70 cm.; O_2/aldehyde, 4.00			$P_{ald.}$, 20.00 cm.; O_2/aldehyde, 2.52		
Time	$-\Delta P$	Per cent ΔP	Time	$-\Delta P$	Per cent ΔP
minutes	*cm.*		*minutes*	*cm.*	
0	0	0	0	0	0
0.5	0.12	1.2	0.5	0.60	3.0
1	0.28	2.9	1	1.80	9 0
1.5	0.45	4.6	1.5	3.85	19.3
3	1.34	13.8	2	4.60	23.0
4.5	2.05	21.1	3	6.65	33.3
7.25	3.24	33.4	4	8.15	40.8
12.5	4.65	48 0	10	12.00	60.0
18.5	5.70	58 8	20	14.50	72.5
28.5	6.50	67 0	30	14 85	74.3
73.5	7.25	74 8	40	14 96	74.8
1680	5.05	52.1	50	14.60	73.0

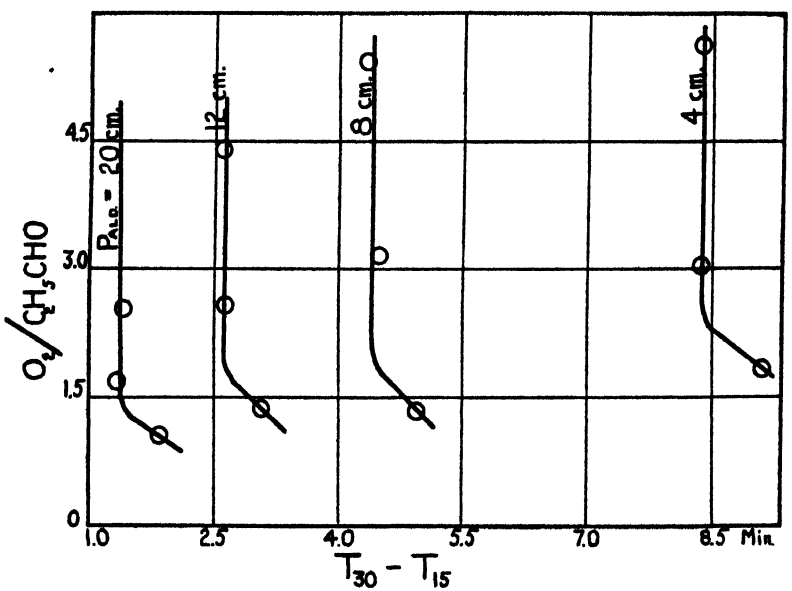

FIG. 2. EFFECT OF OXYGEN CONCENTRATION
Temperature, 150.8°C.

Figure 3 shows the effect of varying the aldehyde concentration while the oxygen concentration is kept constant. The values are given in the form of a log–log plot. From the slopes of the lines the order with respect to

aldehyde is found to be between 1.8 and 2.1. Hence, provided the oxygen concentration is not too low, the rate can be approximately expressed by

$$-\frac{d(C_2H_5CHO)}{dt} = K(C_2H_5CHO)^2$$

TABLE 3

Reaction rate data

TEMPERATURE	PARTIAL ALDEHYDE PRESSURE	OXYGEN / ALDEHYDE	$T_{30} - T_{15}$
degrees C.	*cm.*		*seconds*
150 8	20 00	2 52	85
150.8	20.00	1 68	80
150 8	20.00	1 05	110
150 8	12.06	4 39	155
150.8	12 00	4 37	156
150 8	12 00	2 58	157
150.8	12 00	1.36	184
150 8	8 00	5 46	260
150.8	8 00	5 75	260
150.8	8 00	3 17	270
150.8	8.00	2 10	256
150 8	8.00	1.32	297
150.8	4.00	5 64	502
150.8	4.00	3 02	502
150.8	4 00	1.86	546
167.4	12 00	3.00	76
167.4	8.00	4 00	128
139.1	20.00	2.86	134
139 1	20.00	1.62	144
139 1	20.00	1.62	142
139 1	12.00	3.54	280
139.1	12 00	2 42	282
139.1	8 00	3 20	508
125.3	20 00	1.96	260
125.3	20.00	2 87	266
150.8	8.00	2.58*	320
150 8	20.00	1.17*	111

* Nitrogen added in an amount equal to that of the oxygen.

The temperature coefficient

The temperature coefficient of the reaction has been inferred from three series of runs at constant aldehyde pressures of 20, 12, and 8 cm., using

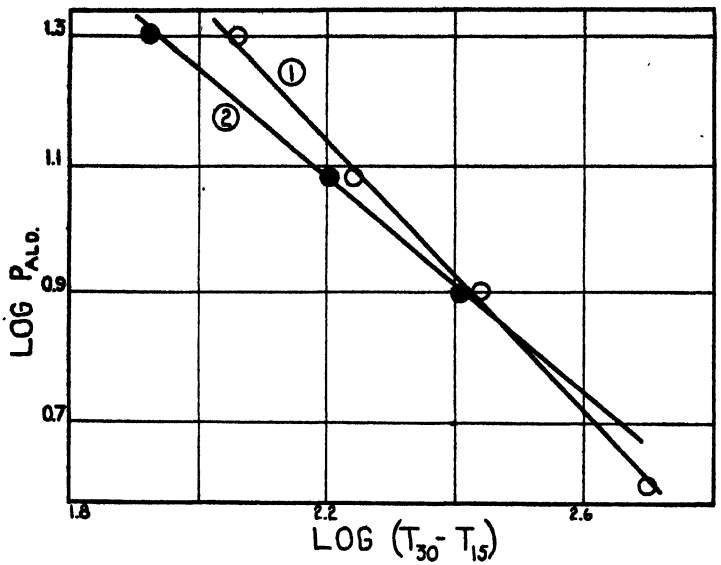

FIG. 3. EFFECT OF PROPIONALDEHYDE CONCENTRATION

Temperature, 150.8°C. Curve 1, P_{O_2} = 20 cm. Curve 2, P_{O_2} = 40 cm.

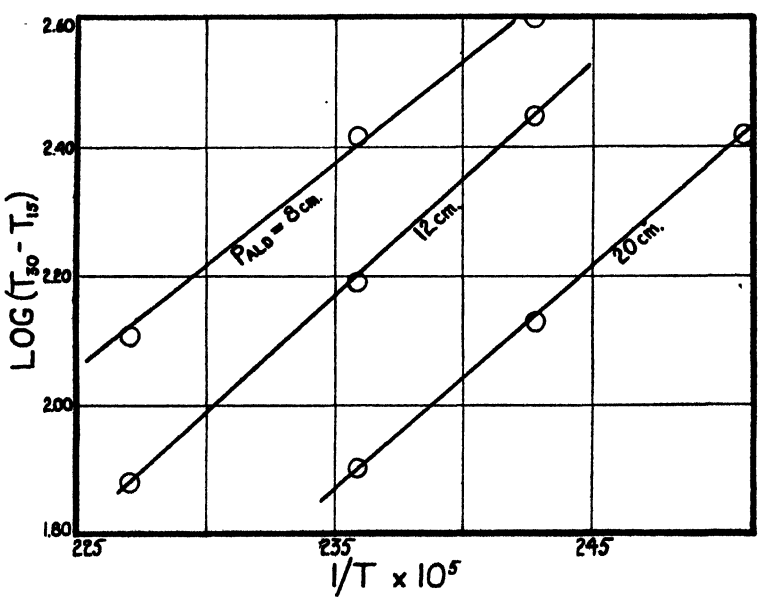

FIG. 4. TEMPERATURE COEFFICIENT

oxygen–aldehyde ratios in the region in which the rate is almost independent of oxygen. The results are shown in figure 4, in which log

$(T_{30} - T_{15})$ is plotted against the reciprocal of the absolute temperature. From the slopes of the lines we obtain the following values for the apparent heat of activation:

$P_{aldehyde}$	*E in calories per gram-mole*
20 cm.	15,700
12 cm.	16,200
8 cm.	14,400
	Mean = 15,400

The products of the reaction

Some analyses of the gaseous products of the reaction are given in table 4. In order to refer the quantities of gaseous products back to the partial pressures which they exerted in the reaction vessel, runs were made with the

TABLE 4

The gaseous products of the reaction

TEMPERATURE	ALDEHYDE PRESSURE	OXYGEN-ALDEHYDE RATIO	O_2	CO_2	CO	$\frac{CO_2}{CO}$
degrees C.	*cm.*		*per cent*	*per cent*	*per cent*	
152	20.0	1 20	47	27	13	2 1
153	20 0	2 05	78	9	5	1.8
150	20 0	1 16	51	27	13	2 1
151	20 0	1 35	66	17	7	2.4
139	30 2	1 60	73	13	5	2 6
139	30 0	1.54*	55	34	4	8 5

* Reaction mixture allowed to stand at 139°C. for 15 hours.

addition of definite amounts of nitrogen. Thus two runs at 150.8°C. with oxygen–aldehyde ratios of 1.16 and 1.35 gave the following results:

(a) $1C_2H_5CHO + 0\ 98O_2 = 0\ 11CO_2 + 0.05CO + 1\ 00$ Condensable
(b) $1C_2H_5CHO + 0\ 87O_2 = 0\ 13CO_2 + 0\ 05CO + 0\ 94$ Condensable

Hence, from a material balance, we find that the condensable products consist of (a) $C_{2.84}H_6O_{2.69}$, and (b) $C_{2.82}H_6O_{2.43}$. On chemical grounds the most probable product is propionic acid. On the basis of the carbon above, this has the formula $C_{2.82}H_{5.64}O_{1.88}$. This leaves unaccounted for (a) $H_{0.36}O_{0.81}$, and (b) $H_{0.36}O_{0.55}$. If a small amount of complete oxidation occurred, it would result in an amount of water equal to the $CO + CO_2$, i.e., 0.16 and 0.18 H_2O, respectively. This is in exact agreement with the hydrogen unaccounted for above. We still have unaccounted for (a) $O_{0.63}$, and (b) $O_{0.37}$. This can obviously be accounted for by assuming the formation of some perpropionic acid. This would have the formula

$C_{2.82}H_{5.64}O_{2.82}$. If the excess oxygen were used in this way, we would have (a) 67 per cent perpropionic acid, and (b) 40 per cent perpropionic acid. The overall reaction is therefore

$$\text{(a)}\ 1C_2H_5CHO + 0.98O_2 = 0.11CO_2 + 0.05CO + 0.16H_2O + 0.56C_2H_5COOOH + 0.28C_2H_5COOH$$

$$\text{(b)}\ 1C_2H_5CHO + 0.87O_2 = 0.13CO_2 + 0.05CO + 0.18H_2O + 0.30C_2H_5COOOH + 0.46C_2H_5COOH$$

The presence of acids in the condensable products was confirmed by carrying out a run at 150.8°C. and removing the reaction bulb. The bulb was then thoroughly washed with distilled water and the washings titrated with 0.05 *N* sodium hydroxide. The results indicated approximately 1 molecule of acid for each molecule of aldehyde disappearing, as required by the above scheme.

A similar experiment was then carried out, the washings being analyzed for per acids using a neutral solution of potassium iodide and titrating the liberated iodine with 0.05 *N* sodium thiosulfate. Approximately 50 per cent of the total acid was found to be per acid, again confirming the above scheme.

In addition to the above products, traces of esters were detected by their odor. It has previously been shown (2) that ethyl propionate is a product of the decomposition of perpropionic acid. The formation of this compound would be accompanied by the formation of carbon oxides and water in equal quantities, and hence necessitates no modification in the above calculations.

Hence the predominant reaction under investigation is

$$C_2H_5CHO + O_2 = C_2H_5COOOH$$

followed by the formation of propionic acid from the per acid, or from a reaction between the per acid and the aldehyde.

The effect of surface

Runs were also made in a bulb packed with short lengths of Pyrex tubing, so as to increase the surface–volume ratio to about six times its former value. It was found that the reaction process was completely altered in the packed bulb. Aging effects were noticed, but after the surface had reached a steady condition it was found that the reaction now led to a pressure increase of about 15 per cent. It therefore appears that the chain process in the empty bulb has been wholly or partially replaced by a heterogeneous reaction.

It has previously been shown that in the empty bulb the pressure after its initial decrease then slowly rose again. As shown by table 4, this increase in pressure was accompanied by the production of a large amount of

carbon dioxide. Analyses of the products from runs in the packed bulb, where there was also a pressure increase, showed the same preponderance of carbon dioxide. It thus appears probable that the secondary process in the empty bulb is also a surface reaction.

Explosions

There was no evidence of any critical explosion limits. Increased temperature and aldehyde concentration caused a progressive increase in the rate without any sign of a discontinuity.

DISCUSSION

As shown above, the main reaction is the oxidation of propionaldehyde to the per acid, followed by the formation of propionic acid from the per acid. The formation of the per acid would lead to a pressure decrease of 100 per cent, while the formation of propionic acid would give 50 per cent. Both reactions must thus occur, since the observed pressure decrease is about 75 per cent, but they are not necessarily independent processes. This point will be referred to again later.

There is no doubt that the main process involved is a chain reaction. This is shown by analogy with other gaseous oxidation reactions, and also by the characteristic form of the differential equation expressing the rate.

The heat of activation is 15,400 calories. This is considerably lower than that corresponding to a bimolecular reaction proceeding at an equal rate in the same temperature range. This, however, is a quite common characteristic of a chain reaction, since the heat of activation is a composite one and includes the temperature coefficient of the chain length.

One common criterion of a chain process is the suppression of the reaction by packing. In this case little information can be obtained from the results in the packed vessel, since the course of the reaction is completely altered. It appears, however, that the deactivating effect of the walls is not very pronounced. This is shown by the reproducibility of the results, and by the fact that inert gases, including excess oxygen, have little influence on the rate.

The mechanism of the reaction

As we have seen the rate of the reaction is given by

$$-\frac{d(C_2H_5CHO)}{dt} = K(C_2H_5CHO)^2$$

On the basis of the Bodenstein scheme (1) for the oxidation of acetaldehyde we have

$$A = A^* \quad (1)$$
$$A^* + O_2 = P^* \quad (2)$$
$$P^* = A^* + O_2 \quad (3)$$

$$P^* + A = P + A^* \quad (4)$$
$$P^* + K = P + K^* \quad (4)$$
$$P^* + O_2 = P + O_2 \quad (5)$$
$$P^* = P \text{ (wall)} \quad (6)$$

where A represents aldehyde, P per acid, and K a negative catalyst.

In the absence of a negative catalyst, this leads to

$$-\frac{d(A)}{dt} = \frac{K_1K_4(A)^2}{K_5(O_2) + K_6K_5^2}$$

This equation disagrees with the experimental results in that it ascribes a retarding effect to oxygen. The only way to avoid this would be to assume that $K_6K_5^2$ is very much greater than $K_5(O_2)$. This, however, is not here a valid assumption since it has been found that the wall effect (K_6) is small.

Any attempt to get over this difficulty by making minor modifications in the scheme is impossible. On the Bodenstein scheme the only fate of A* is to react with oxygen. Hence oxygen exerts no favorable effect on the chain propagation to balance its deactivating effect, and thus it will always appear in the denominator.

To avoid this difficulty it is necessary to make a fundamental alteration in the initiation step, as follows:

$$A + O_2 = P^* \quad (1)$$
$$P^* + A = P + A^* \quad (2)$$
$$A^* + O_2 = P^* \quad (3)$$
$$P^* + O_2 = P + O_2 \quad (4)$$
$$P^* = P \text{ (wall)} \quad (5)$$

The alteration made here is to abandon the assumption of independent activation of the aldehyde, and substitute the more usual idea of an initial bimolecular step. Whence we have

$$-\frac{d(A)}{dt} = K_1(A)(O_2) + K_2(P^*)(A)$$

Evaluating the concentrations of unstable intermediate substances by equating their rates of formation and destruction in the steady state, we obtain

$$-\frac{d(A)}{dt} = K_1(A)(O_2) + \frac{K_1K_2(A)^2(O_2)}{K_4(O_2) + K_5}$$

Neglecting K_5, since the wall effect is small, and dropping the first term, since the chain-starting step is negligible compared to the chain-carrying step, we have finally

$$-\frac{d(A)}{dt} = \frac{K_1K_2(A)^2}{K_4}$$

which agrees with the experimental results.

It has been previously mentioned that propionic acid is also formed. If this results from a secondary decomposition of the per acid, the formation of the per acid will be the rate-determining step, and the above equation will still hold.

It is, however, possible that propionic acid arises from the reaction of aldehyde and per acid, as an integral part of the chain process. If so, we can account for the observed concentration relationships by the addition to the above scheme of the following steps:

$$P^* + A = S^* + S \tag{6}$$
$$S^* + A = S + A^* \tag{7}$$

where S represents propionic acid. This leads to the final equation

$$-\frac{d(A)}{dt} = \frac{2K_1K_6(A)^2}{K_4}$$

which is again of the right form. It seems likely that this is the way in which propionic acid arises, since a straight decomposition of perpropionic acid does not normally yield propionic acid (2).

The oxidation of acetaldehyde

As mentioned at the outset, it was hoped that this work might throw some light on the oxidation of acetaldehyde. It turns out in fact that the propionaldehyde oxidation is essentially similar to that of acetaldehyde, but lacks most of its complications. Thus both give per acids as the primary product. Both are accompanied by a pressure decrease, followed by an increase in the later stages. Both reactions have a low apparent activation energy, and there is no doubt that they proceed by chain mechanisms.

In addition the concentration terms in the expression for the rate are strikingly similar for both. Thus the propionaldehyde reaction rate is proportional to the square of the aldehyde concentration and independent of that of oxygen, while the acetaldehyde reaction is proportional to $(\text{aldehyde})^{1.7}$, and independent of oxygen.

The objections to the Bodenstein mechanism outlined above apply with equal force to the acetaldehyde oxidation. In view of the great similarity of the two reactions there is little doubt that they proceed by analogous mechanisms. It is therefore suggested that the scheme outlined above applies also to the main chain process in the acetaldehyde oxidation.

The acetaldehyde oxidation, however, is complicated by a pronounced induction period. A similar effect is noticed in the propionaldehyde oxidation in the first few runs in a new reaction vessel. When the walls have aged (presumably owing to irreversible adsorption of products), the induction period practically disappears. It is apparent therefore that the

induction period with acetaldehyde may be explained by assuming that poisoning of the walls is a necessary preliminary to the propagation of chains.

SUMMARY

The kinetics of the oxidation of gaseous propionaldehyde have been investigated from 120°C. to 170°C. by a static method. The reaction is a chain process and is similar to the oxidation of acetaldehyde. The rate is proportional to the square of the aldehyde concentration, and independent of that of oxygen. The apparent heat of activation is 15,400 calories per gram-molecule.

The following mechanism is suggested for the oxidation of aldehydes:

$$\begin{array}{lll} \mathrm{RCHO} + \mathrm{O_2} & = \mathrm{RCOOOH^*} & (1) \\ \mathrm{RCOOOH^*} + \mathrm{RCHO} & = \mathrm{RCOOOH} + \mathrm{RCHO^*} & (2) \\ \mathrm{RCHO^*} + \mathrm{O_2} & = \mathrm{RCOOOH^*} & (3) \\ \mathrm{RCOOOH^*} + \mathrm{O_2} & = \mathrm{RCOOOH} + \mathrm{O_2} & (4) \\ \mathrm{RCOOOH^*} & = \mathrm{RCOOOH}\ \text{(wall)} & (5) \\ \mathrm{RCOOOH^*} + \mathrm{RCHO} & = \mathrm{RCOOH^*} + \mathrm{RCOOH} & (6) \\ \mathrm{RCOOH^*} + \mathrm{RCHO} & = \mathrm{RCOOH} + \mathrm{RCHO^*} & (7) \end{array}$$

In the absence of deactivation at the wall, this leads to

$$-\frac{d(\mathrm{RCHO})}{dt} = \frac{2K_1K_6(\mathrm{RCHO})^2}{K_4}$$

in agreement with experiment.

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A STUDY OF THE INFLUENCE OF CAPILLARITY ON THE MELTING POINT OF IODINE[1]

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Received April 26, 1934

This study was undertaken with a view to accumulating additional evidence to support the capillary theory of adsorption (7). It was thought that support of the theory might be gained by the study of the adsorption of substances above and below the melting point. The reasoning was as follows: Above the melting point the adsorbed material would be in the liquid state and consequently the probability of its wetting the adsorbent would be greater than if it were in the solid state. If wetting occurred, then the curvature of the adsorbed material in the minute pits or capillaries of the adsorbent would be such as to produce a decrease of vapor pressure due to the tendency of the free surface energy to assume a minimum value. From this reasoning, it would be expected that the adsorption of vapors should increase at the solid–liquid transition point of the material adsorbed. In other words, the adsorption isotherm should exhibit a decided break in the curve at or above the melting point of the adsorbate.

The next question raised was that concerning the melting point of substances in small capillaries. Inasmuch as capillarity greatly influences the vapor pressure of highly curved surfaces, it follows immediately that the melting point must also be different in such a state than it is in bulk. These questions have been treated in detail in a later section of this paper. In this connection it is interesting to note that a recent paper by Kubelka (4) discusses this same subject. This article came to our attention after the completion of our experimental work.

Studies on solid adsorption (3) in which the adsorbent was kept well below the normal melting point of the substance adsorbed have been conducted in this laboratory. In the present work the adsorbent (silica gel) was kept below and above the normal melting point of the substance (iodine) adsorbed.

In order to facilitate the measurements a quartz fiber balance which has been described by McBain and Bakr (6) and by Cameron (1) was employed.

[1] From the dissertation submitted by W. E. Land to the Faculty of Philosophy of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

APPARATUS

The apparatus used in these measurements is represented diagrammatically in figure 1. The balance and gel were contained in a large glass tube, A, mounted in an air thermostat, T. A glass support, B, having sealed-in iron rods, on which the platinum bucket containing the gel rested, could be raised and lowered by means of a solenoid. This device was used so that the gel could be activated at rather high temperatures without affecting the balance. One hook of a small cylinder, C, supported the fiber balance, while the other was used for lowering in place with the aid of a thread or wire.

A second air thermostat, T′, contained the substance to be adsorbed in a 50-cc. flask, D. The purpose of a similar flask, E, will be explained later. The glass tubing connecting tube A with flask D was wrapped with nichrome wire and heated electrically to prevent condensation of vapors. For

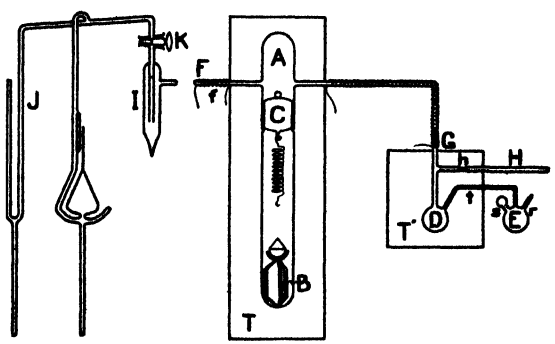

FIG. 1. APPARATUS USED

the same reason it was also heated from the thermostat, T, to constriction, f. This tubing contained an inner seal, G, which was broken at the proper time by a small pointed glass tube containing a sealed-in iron rod. The latter was raised to a suitable height by a magnet and allowed to fall on the seal. The side arms, F and H, were constricted so that they could be readily sealed from the pumps. Omission of stopcocks from the essential parts of the adsorption apparatus was necessary for two reasons: (1) continuous heating of glass; (2) action of vapors on grease. A trap, I, surrounded with a mixture of ether and dry ice, was inserted between the parts to be evacuated and the U-tube, J. This trap prevented the diffusion of foreign vapors and allowed the iodine to be distilled from the flask D to the trap I. In this manner the vapor of this substance could be swept through the apparatus.

The temperature of thermostats T and T′ (figure 1) was automatically controlled within ±0.2°C. by a mercury regulator and heating unit.

Thermometers used for both thermostats were calibrated. A motor-driven stirrer produced the necessary circulation.

The dimensions of the spring used in this work were as follows: average diameter of fiber, 0.010 in.; diameter of coils, 2 cm. The number of coils was twenty-seven. To relieve any strains, this spring, with an added load of about 0.5 g., was annealed for three days at 280°C.

The container for the adsorbent and also for the weights used in the calibration was made from platinum foil 0.0005 in. in thickness. This foil was made into a small bucket, the handle of which was No. 32 platinum wire. The finished bucket weighed 0.28+ g.

Preliminary experiments were conducted to determine whether there was any reaction between the platinum foil and the substance (iodine) adsorbed. Under the experimental conditions no appreciable reaction was detected.

The balance was calibrated over a period of one month at temperatures which covered the experimental range, and the initial and final calibrations were within experimental error. Since the cathetometer used for measuring the extension of the balance could be read to within 0.03 mm., differences in weight of 0.1 mg. could be estimated.

A McLeod gauge, with which pressures of 10^{-6} mm. could be read, was used to determine the degree of evacuation before sealing. Two mercury diffusion pumps, connected in series, and an oil pump, with suitable traps, were used in all cases to obtain a high vacuum.

EXPERIMENTAL

Commercial silica gel, the particles of which were of uniform size, was selected and purified in the following manner. The gel was treated with concentrated nitric acid and heated, with constant stirring, to the boiling point. The nitric acid was poured off after the gel settled. This was repeated several times to remove large foreign particles. It was then refluxed with concentrated nitric acid for three days, washed with distilled water for several days, and dried in an oven at 110°C.

Mercury used for the McLeod gauge, etc., was carefully cleaned and distilled. Chemically pure iodine was further purified according to the method of Lundell, Hoffman, and Bright (5).

The purified gel, contained in an evaporating dish, was partially activated by placing it in a cylindrical furnace continuously heated to 320°C. A stream of nitrogen gas, dried with sulfuric acid and calcium chloride, was passed over the heated gel for two days. About 0.5 g. of this gel, weighed in the platinum bucket, was lowered on support B (figure 1) into a long glass tube, A, having two small side arms. The balance hanging on the support C was next lowered in place and the top of A closed. Connections with this tube were then made as shown in figure 1.

The system was evacuated to the inner seal, G, through side arm, F.

During this evacuation the gel was heated to about 350°C. by a small cylindrical furnace. Since it is very necessary to remove permanent gases, all glass tubing was continuously heated at temperatures higher than those at which adsorption isotherms were run. Evacuation and activation of gel usually required from three to five days. The McLeod gauge showed the pressure to be 5×10^{-6} mm. of mercury before constriction f was sealed.

In order to remove moisture before the introduction of iodine, the remainder of the system was baked and evacuated through the side arm H. This part of the system was then disconnected from the pumps by closing stopcock K. To exclude moisture, capillary r was broken through rubber tubing connected with two calcium chloride towers. A thin glass bulb on the side arm s was next broken and an excess of pure dry iodine quickly introduced into flask E. After having sealed both capillary r and side arm s, flask D was surrounded with dry ice. To remove permanent gases, the pumps were kept running while the iodine was being distilled. By gently heating E with an incandescent lamp, this distillation required about four hours. Flask E was then sealed off at constriction t, and the evacuation continued for several days. With the McLeod gauge showing about the same pressure as above, constriction h was sealed.

The bucket containing the gel was then hung on the balance and the weight of activated gel obtained from the extension it produced.

After the thermostat containing the gel was brought to the desired temperature and the iodine was surrounded with a mixture of ether and dry ice, the inner seal, G, was broken. There was no weighable adsorption at this temperature. The influence of the variation in the pressure of the iodine upon the amount of adsorption was studied by varying the temperature of the iodine. The iodine was first surrounded with a mixture of ice and water. Higher temperatures, chosen to give suitable points on the adsorption curves, were obtained by means of thermostat T′. In order to prevent ordinary distillation of the vapor, it is always necessary to keep the gel at a slightly higher temperature than the iodine.

Values given in the literature (2) enabled a vapor pressure–temperature curve to be plotted, from which the pressures of iodine at these temperatures were obtained.

Before each run the system was reëvacuated and the gel activated. This was accomplished by renewing the side arm F. It is not necessary to replace the broken inner seal, G, since the gel can be completely desorbed by surrounding the iodine with an ether–dry ice mixture. This arrangement also permitted iodine vapor to be swept through the system.

Adsorption isotherms were obtained at 70°, 92.5°, and 115°C. Immediately after the maximum adsorption was reached, for a particular run, the gel was desorbed by decreasing the temperature of the iodine. In each case, several values were obtained which agreed, within experimental error, with those for the adsorption process.

An isobar was obtained by keeping the temperature of the iodine constant and varying that of the gel. The vapor pressure of the iodine corresponding to this constant temperature was 17 mm.

The same sample of gel was used for these runs.

TABLE 1

Adsorption of iodine

p	x/m	p	x/m
mm. Hg		*mm* Hg	
T = 70°C.; weight of gel sample = 0.5700 g.		T = 115°C.; weight of gel sample = 0.5700 g.	
0.03	0 0004	0 97	0.0014
0.471	0 0035	1 95	0 0030
1.03	0 0075	2 90	0 0039
1 50	0 0105	4 75	0 0060
2 16	0 0144	6 80	0 0077
2 95	0 0179	8 90	0 0102
4 31	0 0277	11 02	0 0126
Desorption		13 50	0 0158
2.16	0.0144	15 00	0 0170
1.03	0.0088	16 75	0 0189
0 03	0 0009	18 50	0.0210
		20.45	0 0236
		22 90	0 0268
		24 40	0 0280
		32 00	0 0360
		Desorption	
		20 45	0 0233
		15 00	0 0175
		8 90	0 0119
Run No. 2. T = 92.5°C.; weight of gel sample = 0.5700 g.		Run No. 3. T = 92.5°C.; weight of gel sample = 0.5700 g.	
1.03	0 0040	2 05	0 0072
2.05	0 0074	6 95	0 0202
2 90	0 0095	11 02	0 0316
4 60	0 0142	13 50	0 0385
6.95	0 0202	15 10	0 0453
9 75	0 0272	16 30	0 0561
11 02	0 0312	18 65	0 0702
13.10	0 0378	20 80	0 0800
14.85	0 0438	23 30	0.0982
15.00	0 0456	24 70	0 1105
16.95	0.0575	Desorption	
16.95	0 0596	16.30	0.0655
Desorption		11 02	0 0319
11.02	0 0316		
6.95	0 0204		
2.90	0 0102		

RESULTS

The results of this investigation are given in tables 1 and 2. In each table the column headed x/m gives the grams of adsorbed material per

TABLE 2

Adsorption of iodine

Pressure of iodine = 17 mm.; weight of gel sample = 0.5700 g.

T	x/m
degrees C.	
85	0.0930
92.5	0.0591
100	0.0368
115	0.0198
130	0.0114
137.5	0.0088

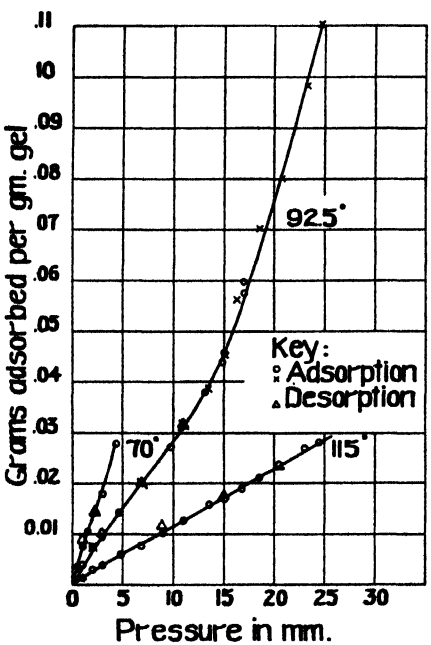

FIG. 2. IODINE ISOTHERMS

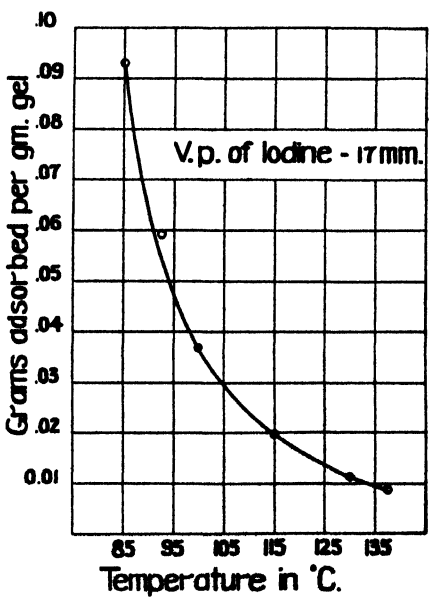

FIG. 3. IODINE ISOBAR

gram of gel and the column headed p gives the equilibrium pressure in millimeters of mercury.

Table 1 gives the results for the three iodine isotherms at 70°, 92.5°, and 115°C., using the same sample of gel. In this way comparable results can

be obtained. Figure 2 shows graphically the results of the first table. It is to be noted that a decided break in the curve of the 92.5°C. isotherm occurs at a pressure of about 11 mm. The curve of the 70°C. isotherm also bends noticeably upwards.

In table 2 are given the results of keeping the pressure of the iodine constant (17 mm.) and varying the temperature of the gel. These results are shown graphically in figure 3. This isobar is a smooth curve showing the normal behavior, i.e., a decrease in adsorption with an increase in temperature. The value of the water content of the gel was found to be 2.3 per cent.

DISCUSSION

The experimental work was performed in such a manner as to lead us to believe that we were in all cases dealing with true equilibrium phenomena. This criterion of real equilibrium is important, as so much erroneous adsorption theory has been drawn from faulty experimental data.

Our experiments show that the adsorption of iodine vapor decreases as we increase the temperature. This is normal behavior and is not in accord with the postulate that we proposed at the outset of this work. We expected to find an increase in the adsorption of iodine vapor above the normal melting point of iodine. However, we did observe a decided increase in adsorption in the case of the 92.5°C. isotherm when the pressure of the iodine exceeded 11 mm. We shall limit our discussion to this isotherm, inasmuch as experimental conditions made it possible for us to work over a sufficient range of pressures only at this temperature. Our explanation of the increase of adsorption at 11 mm. pressure on the 92.5°C. adsorption isotherm is that, at this pressure and temperature, liquid iodine is present in the capillaries of the silica gel, notwithstanding the fact that the ordinary melting point of iodine is 21.5°C. higher. It is to be noted that our quantitative calculations must necessarily be clothed with considerable uncertainties, owing to our lack of knowledge of the physical constants of matter in the state of highly curved surfaces. In other words, it is not safe to assume that the density, surface tension, or latent heat of vaporization of liquids in very small capillaries are the same as the normal values.

Let us consider the case of solid iodine in contact through the vapor phase with liquid iodine wetting a small capillary. The problem is to find the temperature at which the two phases of iodine have the same vapor pressure. It is known that the surface energy of the liquid iodine will operate in such a manner as to reduce the vapor pressure of the liquid. Consequently, the temperature of the solid iodine must be reduced below the normal melting point (114°C.) in order to maintain equilibrium. If we assume that the solid iodine is not affected by capillary forces while the liquid iodine is, the thermodynamic treatment is as follows:

The change in free energy of the solid and liquid (denoting the states respectively by the subscripts s and l) is,

$$dF_s = \left(\frac{\partial F}{\partial T}\right)_p dT = -S_s dT$$

$$dF_l = \left(\frac{\partial F}{\partial T}\right)_p dT + \left(\frac{\partial F}{\partial p}\right)_T dp$$

$$= -S_l\, dT + V_l\, dp$$

At the melting point $dF_s = dF_l$. Here dp is the change in the hydrostatic pressure on the liquid and we shall denote it by $d\pi$,

$$V_l\, d\pi = (S_l - S_s)\, dT$$

$$V_l\, d\pi = \frac{L_F}{T}\, dT$$

Integrating this expression between the limits π_1 and π_2 and T_1 and T_2,

$$V_l\,(\pi_2 - \pi_1) = L_F \ln \frac{T_2}{T_1}$$

In other words, we are able to calculate the temperature to which the system must be lowered in order to maintain equilibrium when the liquid iodine is under a known pressure.

We are also able to calculate the pressure under which the liquid iodine finds itself, owing to the action of the capillary forces, by making use of the well-known thermodynamic equation of Gibbs,

$$\frac{dp}{d\pi} = \frac{v}{V}$$

which expresses the variation of the vapor pressure p, with the hydrostatic pressure π, in terms of the specific volumes of the liquid v, and the vapor V. In our case the anomalous behavior begins at a pressure of 11 mm. and at a temperature of 92.5°C. Inasmuch as the following calculations are only approximate and as we wish to make sure that we are actually dealing with liquid iodine in the pores rather than with a monomolecular adsorbed layer which represents the phenomenon during the first stages of the adsorption, we have selected 20 mm. as the equilibrium pressure in our calculation. Before we can calculate the lowering of the vapor pressure of liquid iodine produced by capillarity, we must first know the vapor pressure of liquid or supercooled iodine at this temperature. This can be found by an extrapolation of the vapor pressure curve of liquid iodine or by means of the Clausius–Clapeyron equation. By neglecting the molal volume of

the liquid by comparison with the molal volume of vapor and by assuming the vapor to be an ideal gas, the integrated form of this equation is,

$$2.3 \log \frac{p_2}{p_1} = \frac{L_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Assuming the normal value for the latent heat of vaporization, 10,500 cal. per mole (International Critical Tables), and substituting the following values in the above equation,

$$p_1 = 90.1 \text{ mm.} \qquad T_1 = 114° + 273° = 387°\text{K.}$$
$$T_2 = 92.5° + 273° = 365.5°\text{K.}$$

it is calculated that liquid iodine at 92.5°C. would have a vapor pressure of 39.8 mm. Extrapolation of the vapor pressure curve of liquid iodine gives the same value. Therefore the lowering of the vapor pressure amounts to (39.8 − 20) or 19.8 mm. Substituting the values,

$$p_2 - p_1 = -19.8 \text{ mm.} \qquad v = \frac{254}{4.0} = 63.5 \text{ cc. per mole}$$

$$\pi_1 = 0$$

$$V = \frac{RT}{p} = 11.4 \times 10^5 \text{ cc. per mole}$$

in the integrated form of the Gibbs equation,

$$p_2 - p_1 = \frac{v}{V}(\pi_2 - \pi_1)$$

gives a negative hydrostatic pressure, π, of 470 atmospheres. To obtain this value, we assumed the density of the liquid iodine in the small capillary to be the same as that of liquid in bulk.

If this approximate value of the negative capillary pressure (470 atmospheres) is now substituted in the equation connecting melting temperature with pressure as previously developed, and where

$$\pi_1 = 0 \qquad V = 63.5 \text{ cc. per mole}$$
$$\pi_2 = -470 \text{ atmospheres} \qquad L_F = 4000 \text{ cal. per mole (I. C. T.)}$$
$$T_1 = 114 + 273 = 387°\text{K.}$$

a melting temperature $T_2 = 323°$K. or 50°C. is obtained. A lowering of the melting point of iodine of 64°C. (114°C. − 50°C.) is indicated.

These calculations lead us to the conclusion that we are completely justified in our contention that it is possible for liquid iodine to exist in a capillary tube in which the vapor pressure of the liquid is only 20 mm. We have seen that our calculations would lead us to the conclusion of a lowering of the melting point of 64°C. This calculated value of the melting point lowering cannot be considered as accurate, owing to our lack of

knowledge of the proper value of the physical constants of liquid iodine in capillaries. We have assumed, for example, the normal density of liquid iodine in the capillaries; this is certain to be incorrect, inasmuch as the very nature of the change in vapor pressure produced by pressure is predicated upon a change in density of the condensed phase.

We have shown that it is possible for the liquid state to have a stable existence far below the normal melting point, provided sufficiently powerful capillary forces are in operation. It is evident that these forces must diminish in magnitude as the adsorption increases, i.e., as the pores fill it is necessary to assume increasing radii of curvature. Therefore, it is necessary to assume the existence of unstable liquid at some point higher on the adsorption isotherm.

SUMMARY

1. Measurements have been made of the adsorption of iodine vapor by silica gel at three temperatures.

2. The adsorption isotherm of iodine at 92.5°C. showed a pronounced flex upwards when a definite pressure was reached.

3. The above behavior was explained by the assumption of liquid iodine being present in the silica gel and wetting the walls of the same.

4. The effect of free surface energy on the solid–liquid transition temperature was thermodynamically explained.

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THE ACTION OF WATER ON THE LATENT PHOTOGRAPHIC IMAGE

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If considerable intervals elapse between the exposure and development of a photographic emulsion kept in a warm humid climate, a flat image is usually obtained. Strauss (5) suggested that water vapor might be the cause of this lack of contrast, and gave experimental evidence to support his view.

The present paper deals with the rôle of water in the above effect.

DESTRUCTION OF LATENT IMAGE BY WATER VAPOR

We have observed that if an Azo emulsion (commercial Azo paper) is exposed to light so as to produce considerable but not maximum developable density, the latent image is either completely destroyed, or reduced to a normal reflection density of less than 0.2 (the actual final value of the density is dependent upon the initial density) by storing the emulsion for several hours in an atmosphere saturated with water vapor at 20°C. The emulsion thus treated is, when dry, capable of yielding very satisfactory prints after a second exposure to light.

In order to eliminate the possibility that some substance other than water vapor was producing the effect, plates coated with an Azo emulsion were stored from twenty-four to forty-eight hours *in vacuo* at a pressure well below 1 mm. They were then exposed to light passing through the walls of the container, and water vapor was introduced by breaking within the container a sealed bulb filled with freshly distilled water. No appreciable difference was noticed in the time required to reduce the latent image to a minimum developable value in the above case than in a similar experiment carried out in the presence of air. A control, stored for forty-eight hours *in vacuo*, exposed as before, and developed, showed that the vacuum storage did not appreciably alter the sensitivity of the emulsion.

Much longer periods of treatment with water vapor are required to destroy latent images (reduced to a developable density of less than 0.2) existing in bromide papers: Eighty hours at 25°C. were required to destroy a latent image produced upon enlarging paper by full exposure to light. An even longer period was required by bromide emulsion film. Slow East-

man process film, given normal exposure to light, showed a marked reduction in density after one hundred and forty-four hours in a saturated atmosphere at 25°C. but complete destruction of the latent image was not effected.

The results of an investigation of the destruction of the latent image by other agents suggests a possible explanation for the action of water vapor. Ether, ethanol (absolute), carbon tetrachloride, carbon disulfide, benzene, and nitrobenzene are without appreciable effect in the vapor phase. Formic and acetic acid vapors and liquid ethylene glycol, however, are even more effective in destroying the latent image than water and, as with the latter, this destruction of the light impression has no effect upon the sensitivity, provided that the treatment is not prolonged beyond the point of complete destruction.

Since the agents found to be effective in destroying the latent image in the same manner as water are of widely different chemical properties, it seems improbable that the effect is chemical in nature. One physical property common to all the effective agents is, however, their ability to soften gelatin in the same manner as does water. Every one of the limited number of substances tried which was without softening action upon the gelatin was likewise without the above effect upon the latent image.

The evidence indicates, accordingly, that the destruction of the latent image by water and by the organic compounds of analogous action is in effect the reverting of the exposed grains to a state not differing greatly (at least photographically) from the original unexposed condition of the grain. The softening of the gelatin greatly facilitates a preëxisting tendency towards reversal of the exposed grain.

Photographic theory assumes that the process of exposure results in the liberation of silver and halogen in equivalent quantities. The liberated halogen is taken up by a "halogen acceptor" which prevents reversal, at least in some measure. Kieser (3) has shown that in the exposure of pure silver bromide grains, reversal predominates to such an extent that a quantum yield of only 1/15th is obtained, whereas in the presence of a suitable acceptor the quantum yield approaches unity. In the case of the usual gelatin emulsion Germann and Hylan (2) have shown by quantitative experiments that gelatin itself probably plays the rôle of the halogen acceptor. A more active acceptor than gelatin might be expected to prevent reversal even by water, and such is found to be the case. Azo F No. 2 paper, soaked for 5 minutes in a solution containing 1 per cent silver nitrate and 1 per cent citric acid, produced upon exposure a latent image which was incapable of destruction by water vapor in the usual way. Moreover, solio paper, in which an excess of silver nitrate again acts as a powerful acceptor, yields upon exposure in the normal manner an image which cannot be destroyed by water-vapor treatment.

When Azo F No. 2 paper, exposed to strong sunlight until highly colored, was treated with water vapor for several hours, the color practically disappeared and only a small density was obtained upon development. This paper was capable of producing an image upon a second exposure, although its speed was reduced by about one-third. When, however, the exposed paper was bathed for 5 minutes in liquid water (which Kieser found to be a suitable halogen acceptor), then dried rapidly and treated with water vapor as before, no decrease in developable density was produced.

Measurements of the time rate of destruction of the latent image (by water vapor of constant pressure) indicate a reaction of the first order.

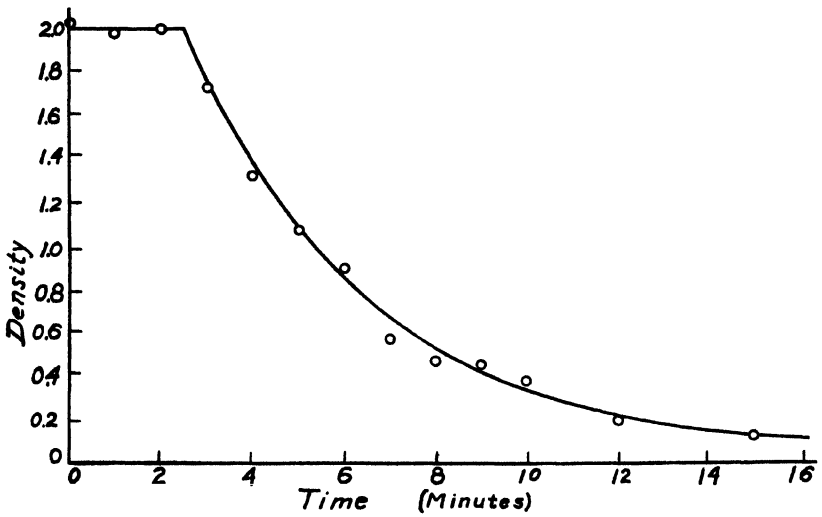

FIG. 1. THE TIME RATE OF DESTRUCTION OF THE LATENT IMAGE BY WATER
The solid line is the theoretical curve

For this investigation Azo No. 1 emulsion coated on glass was used. The data fall very well upon the curve given by the equation

$$X - X_0 = X_m e^{-k(t-t_0)} \tag{1}$$

where X is the density (transmission) at any time t, X_0 is the density when $t = \infty$, X_m is the initial density, t_0 is the time required for the water vapor to penetrate and soften the gelatin, and k is the reaction constant.

The smooth curve of figure 1 is the theoretical curve given by the above equation when $X_0 = 0.05$, $X_m = 2.00$, $t_0 = 2.5$ minutes, and $k = 0.255$.

This equation would be in harmony with the assumption that the water vapor acts chemically upon the development centers of the exposed grains,

Vol. 38, p. 1213. Equation 1 should read

$$X - X_0 = (X_m - X_0)e^{-k(t - t_0)}$$

where the symbols have the meaning given in the article. The theoretical curve in figure 1 was calculated on the basis of the correct equation.

rendering them undevelopable, provided we could assume that the concentration of the water vapor remained constant at the center in question. This assumption, however, would have to be justified. Moreover, if this were the case, we should expect *complete* destruction of the image, regardless of the amount of the initial light exposure. In reality, complete destruction is attained only if the light exposure is small, and the amount of residual density, although always small, increases with the period of exposure. This fact may be explained by the assumption that the greater the exposure, the greater the amount of halogen which has been definitely removed from the sphere of action. This escape of halogen also explains why it is impossible to destroy by water-vapor treatment the image due to age (age mottle).

The destruction of the latent image by water furnishes, perhaps, a partial explanation for the results of Sterry (4) and Cousin (1), who found that the moistened emulsion was less sensitive than the dry one.

THE SENSITIZING ACTION OF WATER

If unexposed Azo F No. 2 emulsion is treated with water vapor for several hours at 25°C. and then dried, the sensitivity of the emulsion is increased. The longer the wave length the more marked is the effect. If the emulsion is first exposed to light so as to produce a high developable density and then treated with water vapor to destroy the image, the sensitivity on second exposure is about the same as that of the water-treated, unexposed emulsion. Figure 2 shows the results of a typical experiment. The curve defined by the triangles is the density–exposure curve for an untreated emulsion. The circles represent the experimental points obtained with an emulsion which had been treated with water vapor for three hours at 25°C. and then dried. The curve defined by the crossed circles was obtained with an emulsion which had been exposed to light to give a near–maximum density, and then treated with water vapor as above. The density from the preëxposure was not completely destroyed by the water-vapor treatment, and an appreciable residual density remained. In order to correct for this, accordingly, it is necessary to shift the curve along the exposure axis until the point of residual density falls upon the normal exposure curve (not shown in figure) for the water-treated, not preexposed, emulsion. The curve thus obtained is shown by the broken line, which falls closely along the points of the water-treated, not preëxposed emulsion.

THE FOGGING ACTION OF WATER VAPOR

If Azo paper is exposed to saturated water vapor at 25–30°C. for several days, considerable developable density or fog is produced. This fog resembles very closely that due to age (age mottle). The action of various

chemical agents on this water fog is the same as that of these agents on age mottle.

Further evidence that water vapor is intimately connected with the age deterioration of paper is given by the following facts. If Azo paper is washed free of soluble salts, the rate of spontaneous deterioration with age

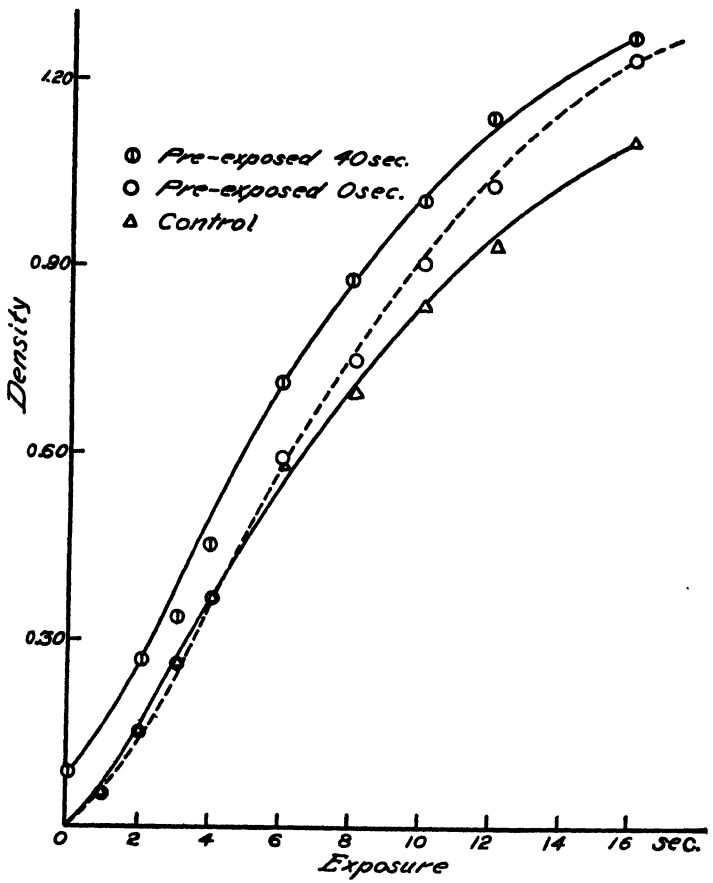

FIG. 2. THE EFFECT OF WATER ON THE SENSITIVITY OF AZO F NO. 2 EMULSION

is increased to such a degree that a measurable developable fog appears after standing in air a few days. We have been able, however, to keep strips of such paper for weeks without fogging by storing them in a desiccator over phosphorus pentoxide, whereas strips of the same paper stored in air at the generally prevailing humidity yielded a normal reflection density of about 1 after a week.

SUMMARY

The phenomenon of the destruction of the latent image by various chemicals in the vapor phase has been investigated. Water vapor is shown to be very effective in destroying the latent image, but formic and acetic acid vapors and liquid ethylene glycol are found to be even more effective. Provided treatment is not carried to a point of complete destruction of the image, there is no consequent effect on the sensitivity. The vapors of ether, absolute ethyl alcohol, carbon tetrachloride, carbon disulfide, benzene, and nitrobenzene have no appreciable effect on the latent image. The very diverse chemical nature of the vapors capable of destroying the latent image would argue against a possible chemical action. The physical property of softening the gelatin similarly to water is common to all the effective agents. It is therefore suggested that the softening of the gelatin greatly facilitates a preëxisting tendency toward reversal of the exposed silver halide grain.

It is shown that water vapor may serve as a sensitizer. Sensitivity is increased more for long than for short wave lengths in the case of Azo F No. 2 emulsion.

A definite relation between age mottle and the water vapor content of the atmosphere is shown to exist.

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THE VISCOSITY OF NITROCOTTON IN VARIOUS SOLVENTS AND MIXTURES

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A previous communication[2] (6) presented a systematic report upon the apparent viscosity of solutions of nitrocotton (12.10 per cent nitrogen) in a large number of solvents and solvent mixtures over periods of time up to one year. Many interesting and significant regularities appeared, of which three may be mentioned. (1) The best solvents give the least viscous solutions with the same nitrocotton, the viscosity being referred to that of the solvent itself in each case. (2) Mixtures are better solvents than pure liquids. (3) The apparent viscosity is largely due to a structural effect,[3] since it is altered by shaking, change of solvent, previous treatment, previous precipitation and recovery of the nitrocotton, and because of its enormous magnitude. All this is additional to any effect of the length of the molecule itself, so much stressed in subsequent years by Staudinger and others. The effects quoted above cannot reasonably be ascribed to alteration in the length of the molecule itself, more especially since changes occur in both directions.

Many questions demanding further study arose, some of which are dealt with in the present report.

EXPERIMENTAL METHODS

The nitrocotton "1919" has been described, together with the method of drying, storage, and preparation of the solutions (6). Units of weight,

[1] The experiments were performed by E. M. G. except where otherwise noted. The work was carried out at Bristol University, England, during the years 1925–27.

[2] The following errata in this article should be noted: p. 321, table V, for methyl phenyl urethane (Smith) the time of standing should be 3.2 hours instead of 32; p. 325, table VII (last column), the slope should be 0.344 instead of 5.589 (this is not a fair comparison as the concentration is so great); p. 326, figure 3, on the figure itself "phenol urethane" should be "phenyl urethane," in the title of the figure "phenyl methane" should be "phenyl urethane" and "ortho tolyl methane" should be "benzyl phenyl urethane"; p. 330, table XI, the viscosity of pure ethyl phthalate (Nobel's; December, 1923) should be 0.04215 instead of 0.4215; p. 333, third line from the bottom, "less impure" should be "less pure."

[3] This was developed as a general explanation of the high viscosity of numerous colloids by J. W. McBain (J. Phys. Chem. **30**, 239 (1926)).

volume, temperature, viscosity, etc. were corrected to absolute standards. Viscosity determinations at 25°C. were exactly as at 55°C., except that the time at 55°C. was 23 hours and 10 minutes before cooling to 25°C. Viscometers were chosen of dimensions to give absolute viscosities with true liquids of the same apparent viscosity as the actual nitrocotton solutions. The results are usually the mean of independent duplicate experiments.

VISCOSITY IN A SERIES OF ACETATES AS SOLVENTS

In the previous communication (7) it was indicated "that molecular weight is an important factor in a series of closely similar compounds. The lower the substance in the homologous series the better the solvent." Also aliphatic substituents appear more favorable than aromatic. One expects the greatest differences with the lowest homologues. These rules appear to obtain with the acetates, although the lowest homologues could not be dried with calcium chloride and were too impure.

It has already been emphasized that impurities greatly affect and generally improve solvent power. Hence for comparison the solvents should be of comparable purity and dried in similar fashion. Otherwise, divergent values are obtained. For example, the solvents were dried with calcium chloride or copper sulfate. The latter, however, introduced a further impurity, presumably sulfur dioxide, which lowered the viscosity, as did sulfur dioxide, the viscosity rising again upon removal of the sulfur dioxide. For example, with isobutyl acetate, the viscosity 0.00643 became 0.00636 after treatment with copper sulfate; 0.00632 after copper sulfate and carbon dioxide; 0.00543 after sulfur dioxide, and 0.00630 after removing most of the sulfur dioxide. Similarly, with isoamyl acetate, 0.00793 became 0.00799 after drying with calcium chloride, and 0.00791 after drying with calcium chloride and copper sulfate.

The solutions were prepared at 55°C. and measured at age 24 hours at 25°C. The data are calculated as in the previous communication, that is, the logarithm of the ratio of the viscosity of a solution to that of the solvent contained therein is divided by the concentration expressed in grams of nitrocotton per 100 grams of solvent. This gives the slope of the graph of the logarithm of the relative viscosity against the concentration, which is, as a first approximation, a straight line. The results are collected in table 1. The source of solvents is indicated as follows: K = Kahlbaum, N = Nobel's, B.D.H. = British Drug Houses, E.K. = Eastman Kodak Co., M = Merck. Purest solvents obtainable from each source were redistilled.

It follows from table 1 that the higher homologues under similar conditions have a value 1.75 ± 0.05. This does not include the aromatic derivative, phenyl acetate, a poorer solvent as indicated by its higher slope, but it does include benzyl acetate with its interposed CH_2 group. Methyl, isopropyl, and butyl acetates are among the most highly sorbed of volatile

solvents, x/m, the sorption expressed in grams, exceeding unity for high relative pressures (5). The number of molecules taken up is greatest for methyl and least for butyl acetate.

TABLE 1

Mean viscosity slopes (log $\eta/\eta_0 \div$ per cent) of approximately 0.5 per cent (grams nitrocotton per 100 grams solvent) nitrocotton in various solvents dried and undried

Prepared at 55°C.; measured at 25.00°C.; age 24 hours

SOLVENT	MEAN VISCOSITY SLOPES		
	Untreated	Dried with $CuSO_4$	Dried with $CaCl_2$
Methyl acetate (K)	1.44	1.12	
Ethyl acetate (K)	1.55		
Ethyl acetoacetate (N)	0.778		
Propyl acetate (K)	1.06		1.72
Isopropyl acetate	1.09	0.832	
n-Butyl acetate (K)		1.05	
Isobutyl acetate (K)	1.16	1.18	1.72
Isoamyl acetate (B. D. H.)	1.16	1.41*	1.77
Benzyl acetate (K; May, 1925)	1.24		
Benzyl acetate (K; March, 1926)	1.66		1.79
Benzyl acetate (K; November, 1926)			1.82
Phenyl acetate (K; May, 1925)	1.92		1.94
Phenyl acetate (K; March, 1926)	2.34		2.35
Phenyl acetate (K; November, 1926)			2.20

* Dried with calcium chloride and then copper sulfate.

TABLE 2

Mean viscosity slopes of approximately 0.5 per cent nitrocotton in solvents at 25°C. and 55°C.

SOLVENT	MEAN VISCOSITY SLOPES		
	At 25°C.	At 55°C.	At 55°C.*
Ethyl acetoacetate (N)	0.778	0.952	0.91
Methylphenylurethan (N; February, 1925)	1.69	1.41	1.61
Ethylphenylurethan (N; February, 1925)	1.58	1.54	1.80
Diethyl carbonate (N)	1.87	1 52	1.58

* Previous communication; different specimens of solvent.

To compare the results in table 1 for acetates too volatile to measure at 55°C. with the solvents previously studied at this temperature, the data in table 2 for solutions at both temperatures are assembled.

It will be noted from the low value of the slopes that the acetates would be classed as good solvents, with the exception of phenyl acetate. For the

last three substances in table 2, the slopes are higher at 25°C. than at 55°C. and the order in the three columns is not identical. This is partly because other samples of a different degree of purity were employed for the last column.

SOLUBILITY AND VISCOSITY IN ALCOHOLS

Methyl alcohol is almost a complete solvent. Ethyl alcohol is such only at very low temperatures, the solution becoming more viscous and setting to a jelly on warming to room temperature.[4] This reversible change cannot, of course, be ascribed to a change in the length of the molecule. Butyl alcohol is a non-solvent and it is sorbed to a far less extent by nitrocotton, not exceeding 5 per cent by weight.

The solubility and slope of nitrocotton were determined in Kahlbaum's methyl alcohol; also in a sample of the latter which had been dried with

TABLE 3

Viscosity and dissolving power in methyl alcohol, ethyl alcohol, and in a mixture of equal weights, at 25.00°C. and age 24 hours

SOLVENT	NITROCOTTON DISSOLVED	DECREASE	VISCOSITY SLOPE	DECREASE
	per cent	*per cent*		*per cent*
Methyl alcohol (K)	91.1		0 620*	
Methyl alcohol (K), dried with $CaCl_2$	85.2		0.654	
Ethyl alcohol	24 1		2.275	
Methyl alcohol (K) + ethyl alcohol	45.4	21	1.199	18

* At age 47 hours.

calcium chloride; also in dry ethyl alcohol and in a 50-50 mixture by weight of undried methyl alcohol and dry ethyl alcohol. In all cases nitrocotton solutions were prepared in the ordinary manner as for measurement at 25°C., but before the viscosity was taken any undissolved fibers were filtered off. Then a known weight of the filtrate was evaporated to constant weight. From this was calculated the percentage of the 0.5 g. of nitrocotton which had dissolved in the 100 grams of solvent. The nitrocotton was, of course, not uniform, and this affords a sensitive test of progressive dissolving power without measuring a true solubility in the ordinary sense. The data are given in table 3.

It will be seen from table 3 that, as was expected and in accordance with

[4] C. W. Hutchinson in our laboratory finds that ether–alcohol (75:25) containing 5 per cent nitrocotton at room temperature forms an opaque gel on heating in a sealed tube to 90°C. The phenomenon is completely reversible, the gel quickly reverting to a fluid sol at room temperature.

our rules, drying[5] diminishes the solvent power of methyl alcohol, as shown both by the increased viscosity and the small proportion of nitrocotton dissolved. On the other hand, the mixture of the two alcohols yields a viscosity as well as a proportion of nitrocotton dissolved which is one-fifth less than that of the arithmetic mean of the two solvents separately.

HIGH MELTING SOLVENTS IN MIXTURES WITH ALCOHOL AND BENZENE

Since seven possible solvents are solid at 55°C., the attempt was made to study them at 55°C. in admixture with ethyl alcohol or benzene. Table 4 presents the results with alcohol. Equal parts by weight of benzene with phenylurethan or diethyl carbonate did not dissolve the nitrocotton. This was likewise the case with one part of phenylacetanilide and three parts of alcohol, and one part of α-pyridylurethan[6] with five parts of alcohol. Some

TABLE 4

Viscosity slopes of solutions of nitrocotton in substances to which an equal weight of ethyl alcohol has been added

Temperature, 55°C.; time, 24 hours

SOLVENT	SLOPE		PER CENT DECREASE
	Pure	Mixture	
Form-*o*-toluidide (N)	1.058	0.870	18
Phenylurethan (N)	1 340	1 04	22
Methylphenylurethan (N; February, 1925)	1 407	0 89	37
Diethyl carbonate (N)	1 524	1 08	29
Ethylphenylurethan (N; February, 1925)	1 535	0 94	39
Ethyl phthalate (E. K.)	1 611	1 27	29

substances previously measured in pure condition are included for comparison.

It has already been pointed out that a small addition, even of a reputed non-solvent, lowers the viscosity and improves the solvent power of any solvent for nitrocotton. Thus at 55°C. even the extreme non-solvent hexane, added in one or two parts per hundred, lowers the actual viscosity slope of the solvent methylphenylurethan by 3 and 6 per cent.[7] Other examples are given in table 4. This is likewise shown in figure 1 for the effect of the semisolvent, ethyl alcohol, upon methylphenylurethan over

[5] For solvents previously studied at 55°C., drying a solvent over phosphorus pentoxide for 14 days at room temperature raised the slope for benzylphenylurethan (N) 8 per cent, leaving that for methylphenylurethan (N; February, 1925), ethylphenylurethan (N; November, 1926), and diethyl carbonate (N) unaffected.

[6] α-Pyridylurethan is insoluble in benzene.

[7] An opposite effect is probably produced upon acetone.

the whole possible range. Beyond 85 per cent alcohol, progressively less of the nitrocotton dissolves, and the true slope cannot be measured, although it must become very high (cf. table 3).

For comparison with the mixtures in table 4 the following results were obtained with similar mixtures of high melting substances: diethyldiphenylurea (N), 0.677; phenyl oxamic ester (N), 1.136; *p*-toluenesulfonanilide (N), 1.110; diphenylurethan (N) (42 g. in 58 g. of alcohol), 0.849.

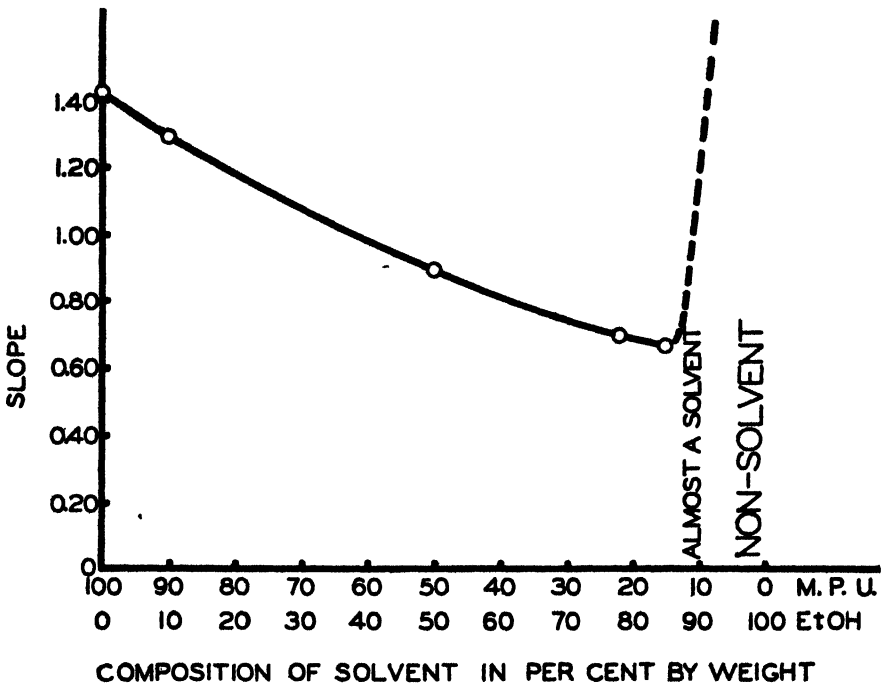

FIG. 1. VISCOSITY SLOPES OF 0.5 PER CENT SOLUTIONS OF NITROCOTTON IN THE SOLVENT METHYLPHENYLURETHAN, TO WHICH THE SEMISOLVENT ETHYL ALCOHOL IS ADDED IN INCREASING AMOUNTS, LOWERING THE VISCOSITY OF THE MIXTURE

Temperature, 55.00°C.; time, 24 hours

With benzene (K) mixtures containing equal parts by weight, the slopes for the mixtures were 0.953 and 1.66 for form-*o*-toluidide (N) and methylphenylurethan (N; February, 1925), respectively, being a decrease of 15 per cent for the former but an increase of 18 per cent for the latter. The slopes for 50 per cent mixtures of benzene (K) with diethyldiphenylurea (N), phenylacetanilide (N), and diphenylurethan (N) were 1.47, 1.45, and 2.10, respectively.

It follows from the data adduced that all are to be classed as good solvents except α-pyridylurethan and phenylacetanilide. These two are

too insoluble even in alcohol and benzene to be given a comparable test. Further, it is to be remembered that the specimens of the high-melting solvents were in most cases not as pure as the standard solvents used for comparison in table 4. Lastly, the relative order is certainly affected by such large additions of alcohol or benzene.

Contrary to expectation, the data indicate that diphenylurethan is potentially a better solvent than phenylurethan.

Besides these and the numerous striking examples of the lowering of viscosity slopes in mixtures given on pp. 325 to 328 of the previous communication (6), three more may be cited; namely, that in table 3, and the 50 per cent mixtures of *n*- and isobutyl acetates (K), and of benzyl with phenyl acetate (K). The slopes for the last two mixtures at 25.00°C. were 1.384 and 2.009, being 13 and 10 per cent less than the means for the respective pure solvents. Further, 50 per cent mixtures of formanilide and form-*o*-toluidide yielded a slope of 0.985 at 1 day and of 0.074 at 80 days, being 7 per cent less than the mean of the values for the two solvents at 1 day, 1.02 and 1.085, respectively.

C. W. Hutchinson in the Bristol laboratory found that the addition of a few per cent of the following impurities did not cause the residue of nitrocotton particles left undissolved by specially purified formanilide (N) to dissolve: aniline (except in certain cases upon prolonged shaking), formic acid, ether, alcohol, 5 per cent ether–alcohol, formamide, benzene, toluene, tartaric acid, citric acid. On the other hand, 2 or more per cent of acetone was successful. Guncotton and another sample of nitrocotton dissolved in the same incomplete manner. Aniline and formic acid by themselves do not affect the appearance of nitrocotton.

PROLONGED PREHEATING OF SOLVENTS

Ethyl phthalate has given us much trouble throughout the many years in which we have studied solutions of nitrocotton therein. (See figure 4, page 335, of reference 6.) The first sample obtained was an excellent solvent with one of the lowest viscosity slopes. Subsequent much purer specimens have given high slopes.

Since in prolonged aging experiments at 55°C. it might be surmised that the solvent itself is changing, different specimens of two solvents were maintained at the very much higher temperature of 130°C. for 7 days in sealed tubes previously evacuated with a mercury pump with a trap containing solid carbon dioxide and ether or liquid air. Where necessary the liquid itself was surrounded by solid carbon dioxide and ether. *o*-Tolylurethan was partially converted to a form with a melting point higher than 130°C. as compared with the original melting point of 45°C. The results given in table 5 were obtained with 0.5 per cent solutions subsequently prepared, aged, and measured at 55.00°C. Each solution was in a separate sealed tube.

Viscosity is distinctly lowered by the previous drastic treatment of the triacetin. The effect is slight with phenoxyacetic ester. With ethyl phthalate a distinct increase results as shown in table 6.

A graph of all these slopes against the logarithm of time yields approximately straight lines, indicating that the viscosity of the solution would fall

TABLE 5

Results obtained in preheated solvents

SOLVENT	VISCOSITY SLOPES				
	24 hours	14 days	42 days	84 days	168 days
Triacetin (N)*	1 225	0.890	0.626	0.373	0.174
Triacetin (N)†	1.023	0.511	0.324	0.226	0.124
Triacetin (K)*	1.230	0.874	0.508	0.362	
Triacetin (K)‡	1 025	0.759			
Phenoxyacetic ester (N)*	1 451	1 038	0 770	0.519	0.283
Phenoxyacetic ester (N)†	1.319	0.976	0.744	0 388§	0.293

* Untreated original.

† Aged seven days at 130°C

‡ Evacuated at 3×10^{-4} mm.; aged seven days at 130°C.

§ One hundred and nineteen days.

TABLE 6

Results obtained with preheated ethyl phthalate as solvent

SPECIMEN	VISCOSITY SLOPES					
	24 hours	7 days	14 days	42 days	84 days	168 days
E. K., untreated	1.664		0 938	0.853	0 507	0.319
E. K., aged*	1 776		1.072	0 778	0.594	0.406
E. K., evacuated, aged	1.81		1 091	0.724	0.571	0.393
E. K.,† evacuated, aged	1 759		0.988	0.736	0.621	0.349
N, untreated	1 637		1.242	0.926	0.703	
N, evacuated, aged	1.750		1.16	0.87	0.66	
E. K. (July, 1927), untreated	1.786	1.347	1.49			
E. K. (July, 1927), evacuated, aged	1 800	1.42	1.298			

* In all cases aging was for seven days at 130°C.

† Trace of nitrocotton added; slight apparent decomposition.

to that of the solvent after 600 to 800 days at 55°C. However, it is worth noting that during prolonged aging some of the nitrocotton definitely separates out from the ethyl phthalate solution. The solutions in triacetin and phenoxyacetic ester would seem to tend towards their end point in 300 to 500 days.

In contrast to experiments on previous heating of the solvent alone were

the experiments previously reported (reference 6, table IV, p. 320) on heating the dry nitrocotton at 60°C. Subsequent experiments, but heating in sealed tubes evacuated to 0.0002 mm., have shown that samples are somewhat erratic, some being only slightly yellow after six months at 60°C. in an evacuated tube, whilst others were brown or reduced to a moist black mass. Where brown fumes appeared after a week, they disappeared again. It was found that the viscosity of solutions in ethyl formanilide, when the nitrocotton had previously been heated for 84 days at 60°C., was only one-eighth of its usual value. These experiments disprove the alternative hypothesis suggested by others that the degradation consists in oxidation of the nitrocotton by the air.

PROLONGED AGING OF SOLUTIONS

In the previous communication[8] it was shown that when solutions of nitrocotton are made up and kept in the dark at 55°C., their viscosity falls approximately with the logarithm of the time over periods of six months to a year. Reasons were given for believing that this was due to degradation or to a physical dismemberment of the cellulose aggregates rather than to denitration of the nitrocotton or nitration of the solvent. These tubes have been kept under observation for further periods up to as much as three years.

In several cases a noteworthy new phenomenon has been observed. Several of these solutions which had been steadily losing their viscosity began to set to jellies. For example, the benzylformanilide solutions (sample 1/10/20, reference 6, p. 333) jellied between the ages 200 to 300 days. These jellies were broken up by shaking at 55°C., but again set to jellies within a few more hours at 55°C. The similar solutions in a later purer sample (16/2/25, reference 6, p. 333) were still fluid at 770 days. Similarly, solutions in ethylformanilide (reference 6, p. 330) began to jelly after 700 days at 55°C. Finally, the solutions in ethyl phthalate (Nobel's; December, 1923; reference 6, p. 330) began to increase in viscosity towards the end of three years. Here again an explanation of these enormous viscosity changes in both directions is not to be sought in a change in the length of the molecule itself. It bears rather the hall-marks of structural viscosity.

The data for these very long periods are given in condensed summary in table 7, the values at 24 hours being included for comparison. The designations of some of the solvents refer to the previous communication. In scrutinizing the data it should be remembered that the viscosity slopes will

[8] Pp. 329–44, especially table XI and figures 5 and 6. Reference should be made to the standard work of Sir Robert Robertson on the slow decomposition of nitrocellulose at 135°C. (ROBERTSON, R., AND NAPPER, S. S.: J. Chem. Soc. 91, 764 (1907)).

TABLE 7

Viscosities of solutions of nitrocotton kept at 55°C. for prolonged periods (measurements by L. E. S. and E. M. G.)

SOLVENT	VISCOSITY SLOPES					
Benzylphenylurethan (March 13, 1924)	Days	1	329	700	986	
	Slope	1.995	0.288	0.219	0.158	
Ethyl phthalate* (Nobel's; December, 1923)	Days	1	326	697	978	
	Slope	2.05	0.55	0.101	0.163	
Ethyl phthalate* (Eastman Kodak)	Days	1	324	661	937	
	Slope	1.97	0.232	0.107	0.112	
Ethylformanilide (May, 1924)	Days	1	328	694	(800)	
	Slope	0.872	0.085	0.047	Jelly-ing	
Ethylphenylurethan (March, 1923)	Days	1	327	690	980	
	Slope	1.80	0.286	0.095	0.048	
Methylphenylurethan (August 8, 1923)	Days	1	326	688	968	
	Slope	1.605	0.246	0.230	0.0748	
Formanilide (Nobel's; May, 1924)	Days	1	328	681		
	Slope	1.02	0.034	0.029		
o-Tolylurethan (April 15, 1924)	Days	1	328	666	941	
	Slope	1.715	0.268	0.107	0.051	
Phenylurethan (August, 1923)	Days	1	330	674	930	
	Slope	1.435	0.115	0.074	0.034	
Phenylurethan† (Nobel's; July, 1925)	Days	1	14	384		
	Slope	1.365	0.78	0.154		
Benzophenone (November, 1923)	Days	1	330	672		
	Slope	1.58	0.277	0.136		
Benzophenone (Kahlbaum)	Days	1	14	138	506	786
	Slope	2.04	1.39	0.915	0.306	0.217
Benzophenone (Nobel's; April 2, 1925)	Days	1	14	139	505	786
	Slope	1.76	1.34	0.94	0.284	0.159

* Particles of nitrocotton separate from the ethyl phthalate solutions after long periods of aging. Some evidence of a similar behavior was noted with acetone.

† Specially purified. Similarly purified formanilide (N) did not dissolve quite all the nitrocotton fibers. The true slope must therefore exceed the observed value, 0.80.

TABLE 7—*Concluded*

SOLVENT	VISCOSITY SLOPES					
Benzophenone† (M)	Days	1	14	387	668	
	Slope	1.56	1.12	0.291	0.196	
Benzylformanilide (February 16, 1925)	Days	1	84	203	572	769
	Slope	1.23	0.345	0.161	0.068	0.053
Diethyl carbonate (N)	Days	1	14	18	373	
	Slope	1.585	0.86	0 69	0.26	
Diacetone alcohol (N)	Days	1	15	19	371	
	Slope	0.82	0.45	0.49	‡	
Ethyl acetoacetate (N)	Days	1	14	367		
	Slope	0.91	0.565	0.055		
Ethyl lactate (N)	Days	1	14	365		
	Slope	1.080	0.830	0.269		
Ethyl benzoate (N)	Days	1	14	363		
	Slope	1.49	1.014	0.283		
Ethyl oxalate (N)	Days	1	348			
	Slope	1.56	0.48			

‡ A 0.4 and a 0.5 per cent nitrocotton solution now exhibit a viscosity 0.00927 and 0.00940, respectively, as compared with the original solvent itself, 0.01383, presumably owing to progressive condensation of the solvent.

become zero when the viscosity of the solutions has fallen to that of the solvent. In no case is this attained or attainable even if only the lowest possible degradation products were left in solution. The lowest final slope is 0.03, where the viscosity is only 3 per cent higher than that of the solvent itself. The initial (logarithmic) slopes were several fold or many fold that of the solvent even for these very dilute (0.35–0.4 per cent) solutions.

The last six more mobile solvents of table 7 were all measured (L. E. S.) subsequent to the previous publication.

SOME DATA FOR ANOTHER SIMILAR NITROCOTTON

Five-tenths per cent solutions were prepared and measured in the usual way at 55°C., using the 1919 and a 1927 sample[9] of nitrocotton with the results given in table 8. The behavior is parallel, and furfural appears as an excellent solvent.

[9] Nitrogen, 12.24 per cent; nitrogen (ash-free), 12.26 per cent; ash, 0.13 per cent; solubility in ether–alcohol, 99.4 per cent.

At room temperature a 7 per cent solution in furfural is almost too viscous to flow. Two solutions of the 1927 sample in amyl acetate (B. D. H) prepared at 55°C. and measured at 25°C. at 1 day contained 2.102 per cent and 4.618 per cent, respectively. Their densities were 0.8685 and 0.8888 and their viscosities 8.828 and 19.49 (falling ball method), giving viscosity slopes 7.57 and 9.52.

TABLE 8

Comparison of viscosities of 1919 and 1927 nitrocotton solutions at 55.00°C.

SOLVENT	NITROCOTTON	VISCOSITY SLOPES				
		1 day	7 days	14 days	42 days	84 days
Ethylphenylurethan (N; November, 1926)	1919	1.472		1.002	0.583	0.312
	1927	2.184		1.405	0.744	0.396
Methylphenylurethan (N; November, 1926)	1919	1.470		0.984	0.727	0.514
	1927	2.243		1.577	0.968	0.467
Phenylurethan (N; May, 1925)	1919	1.433		0.881		
	1927	2.294		1.007		
Phenylurethan* (N; July, 1925)	1927	2.481			0.392	0.217
Furfural (B. D. H.)	1919	1.383				
	1927	1.971	1.829	1.745		

* Specially pure.

DISCUSSION

It is amply established that the viscosity of a solution of nitrocotton in a definite solvent at a definite temperature depends upon a large number of other factors such as previous mechanical treatment, slight impurities, etc. A large part of this behavior must be ascribed to structural viscosity in accordance with the general hypothesis advanced by one of us on a previous occasion (4). It is obviously not to be explained as being due to alterations or fluctuations in the length or size of the cellulose molecule itself.

In general, the solvent power of various solvents may be defined as following the indications of the viscosity slopes; the lower the (relative) viscosity, or rather, viscosity slope, the better the solvent. Thus it would appear from the new data here presented that diacetone alcohol, ethyl acetoacetate, and ethyl lactate[10] are excellent solvents, and that ethyl benzoate and ethyl oxalate are good solvents for this type of nitrocotton.

Degree of solvent power is necessarily inferred from indirect methods, since true solubility in the usual sense is not present. Such indirect methods are the determination of the percentage of nitrocotton dissolved under specified conditions (1), the position of minimum viscosity in mix-

[10] The slope for ethyl lactate (N) at 55°C. and 1 day was 0.86, and after drying was 0.80.

tures (3) (found to dissolve cellulose derivatives most readily), the determination of the amount of a diluent which the solvent can bear (2), and the minimum temperature at which the solvent dissolves the cellulose derivative (2). Others will now be briefly described.

It is a serious complication that in mixtures a liquid chosen as diluent may actually reinforce and improve the solvent power, as in the well-known case of alcohol and ether or of toluene and alcohol for nitrocotton of low nitrogen content (8). The nearest approach to a perfect diluent or a non-solvent is a low-boiling, saturated paraffin[11] such as hexane.

Further methods tried by one of us (L. E. S.) and found promising are as follows:

1. Adding to a diluent a solvent until the nitrocotton is just gelatinized (compare p. 1221). End points are more indefinite with alcohol and chloroform as diluents than with benzene. The addition of only a few per cent of a good solvent converts ethyl alcohol into a solvent. Many times larger amounts are required for chloroform and benzene, but the order of the solvents is not the same in the three cases. Of five tested, acetone and ethylformanilide were most effective with chloroform and benzene, and nitrobenzene least so. Ethylphenylurethan was next best, but excelled with alcohol. This method is less sharp than that of precipitating with diluents, but the results are parallel with those obtained by viscosity measurements.

2. A rapid approximate method is to pour dilute solutions of solvents in hexane upon nitrocotton and to note the very different swelling, greatest for ethylformanilide and least for benzylphenylurethan.

3. The sorption of solvents from solution in hexane by means of nitrocotton may be measured by noting the refractive index of the supernatant liquid by a differential method. Nitrocotton sorbed ethylformanilide most, to an extent exceeding its own weight, but ethylphenylurethan and benzylphenylurethan far less.

4. Finally, if 1 g. of nitrocotton is added to about 15 g. of various liquids, the temperature is raised by about 0.1°C. by non-solvents and by several degrees by good solvents. Others may give intermediate values, and the results are easily distorted if very volatile solvents are employed.

All the varied methods of testing solvent power give in general more or less comparable results. Precise comparison and classification are affected by the very numerous factors involved and the specific properties of the sample of cellulose derivative under test.

Hutchinson compared the times required under comparable conditions for nine solvents just to dissolve 0.5 per cent of nitrocotton. Of these ethyl lactate was by far the quickest, requiring only three-quarters of an hour

[11] E. W. J. Mardles (J. Soc. Chem. Ind. **42**, 132T (1923)) used petroleum spirit (b.p. 90–100°C.).

with slow rocking at 55°C. Taking this time as unity, the other solvents were as follows: ethylformanilide, 5; formanilide, 16; ethyl phthalate, 21; benzylformanilide, 24; ethylphenylurethan, 28; *o*-tolylurethan, 49; benzophenone, 56; benzylphenylurethan, 80. The exact order appears to be of little significance and only very roughly does it parallel the viscosity slopes either immediately after solution or after 14 days or in standard experiments at 24 hours or 14 days at 55°C., ethyl phthalate being a prominent exception.

It should be placed upon record that particles seen in solutions of nitrocotton in ethylformanilide or ethylphenylurethan, when examined even under Zsigmondy's immersion Winkel ultramicroscope, are so few in number that it is certain that the greater part of the nitrocotton is invisible in the highest powers of the ultramicroscope.

The rule that the viscosity slope falls off towards zero in approximate proportion to the logarithm of the time as if the structural viscosity would have disappeared in one or two years appears to be of fairly general application. As would be expected from the hypothesis of dismemberment of nitrocotton micellar aggregates by the solvent, it is independent of the concentration, as was shown by Hutchinson with concentrated solutions in diethyl carbonate and in ethyl lactate; namely, 2.675 per cent and 3.141 per cent nitrocotton, respectively. When first measurable, their viscosities were 42.9 poises at 3 days for the diethyl carbonate solution and for the ethyl lactate 28.9 poises at 3 hours, falling to 6.17 poises at 5 days. Both quickness of dissolving and comparatively low viscosity slope indicate ethyl lactate to be much superior to diethyl carbonate as a solvent. Another 2.3 per cent solution in diethyl carbonate lost in 14 days 92 per cent of the viscosity possessed immediately upon solution. Films made from concentrated solutions in ethyl lactate dried very slowly, whilst those from amyl acetate and diethyl carbonate exhibited tensile strengths (W. B. Lee) of between 8000 and 11,000 lbs. per square inch. Further examination is required to test the effect of time and the possible influence of a skin formation.

SUMMARY

1. Experiments are described with over one hundred solvents and solvent mixtures, some of very high purity. The results confirm and extend our previous findings. They emphasize that the chief factor involved in the apparent or effective viscosity of nitrocotton solutions is structural viscosity due to colloidal aggregates of easily varied degree of ramification and dismemberment.

2. The time experiments at 55°C. were extended to three years, when some of the solutions are approaching the viscosity of the pure solvent within a few per cent, an enormous drop in viscosity. However, in several

cases, the viscosity passes through a low minimum and the solutions may afterwards even set to jellies.

3. Four other new methods of determining degree of solvent power are very briefly indicated.

We have great pleasure in acknowledging the invaluable support and coöperation of Messrs. Nobel's Explosives Co., Ltd., and the unfailing interest of their scientific staff, which have rendered this work possible.

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NEW BOOKS

Conductometric Analysis. By H. T. S. Britton. 14 x 21 cm.; ix + 178 pp. London: Chapman and Hall, Ltd., 1934. Price: 12s. 6d.

Although the suggestion that analytical titrations could be followed by measurement of conductivity was made by Kohlrausch as long ago as 1885, the possibilities of the method did not receive the attention paid to the potentiometric method of titration. The chief reason for this neglect was probably the fact that the accurate measurement of conductivity has been a matter of some difficulty. In recent years, however, as a result of developments in connection with the use of the thermionic valve and of the introduction of other means of producing and rectifying alternating currents, the procedure has been very much simplified, so that the potentialities of the method are being more fully studied. The only collected work on conductometric analysis has hitherto been the excellent monograph *Konduktometrische Titrationen* by Kolthoff, and so the book under review will be welcomed by those who prefer their scientific literature in the English language.

The first two chapters deal with the general theoretical aspects of electrical conductivity; they are followed by two further chapters on conductivity titration apparatus and methods. Although the various principles involved in the measurement of conductivity are adequately discussed, it is strange that no details are given of the actual method of *titration*, since it is essentially different from that used in ordinary volumetric or potentiometric analysis. Sections on the titration of strong and weak acids and bases of various kinds are followed by a discussion of replacement and precipitation reactions, and of the use of mercuric perchlorate as a titrant. The next three chapters deal with abnormal acids, the precipitation of metallic bases and the application of conductometric titration to research; they are more particularly concerned with the author's own work and are of somewhat specialized interest. The book concludes with an interesting, although perhaps too concise, description of industrial applications which serves to show the scope of the conductometric method of analysis.

It is a matter of regret that the author frequently uses the Arrhenius theory of ionization as a basis of his discussion, so that the language is often obsolete and misleading from the modern standpoint; the main principles underlying conductometric titrations are, however, treated quite adequately. The book is well produced and contains a commendable number of clear diagrams which add considerably to its value.

S. Glasstone.

Molekülstruktur. By H. A. Stuart. 22 x 14 cm.; x + 388 pp. Berlin: Julius Springer, 1934. Price: paper, 32 RM; bound, 33.80 RM.

The rapid advances made in recent years in the determination of the shapes and sizes of molecules by modern physical and physicochemical methods have led to a desire on the part of many chemists for a concise and intelligible summary of the results. This is provided very well in Dr. Stuart's book, which is characterized by a satisfactory, though brief, exposition of experimental methods, and the absence of difficult mathematics. These features, together with the numerous tables of numerical results and copious references to the literature, combine to produce a work of

special appeal and service to chemists working in other fields who wish to acquaint themselves with the procedure and data of the new methods. The topics dealt with include the theories of valence and molecular forces, nuclear distances and configurations, electric moment, Raman effect, Kerr effect, electron diffraction, infra-red spectra, proper vibrations, valence angles, potential curves, and dissociation. The treatment, although necessarily brief, is quite sufficient to bring out the main features of the methods, and although many important matters are dealt with in a small space, it cannot be said that the book is in any way superficial. In some cases the treatment lacks completeness, e.g., in the discussion on specific heats of gases no high temperature methods or results are included, and the picture is too much idealized, but on the whole a very fair balance of treatment is preserved, and the indexes are good. The volume is one which can be warmly recommended. It satisfies a definite need in chemical literature.

J. R. PARTINGTON.

Chemie der Enzyme, Pt. 2, Section 3. By HANS V. EULER. 26 x 17 cm.; xi+ 663 pp. München: J. F. Bergmann, 1934. Price: 58 RM.

In this volume, Prof. Hans V. Euler and his colleagues, Franke, Nilsson, and Zeile, cover the chemistry of catalase and the enzymes concerned in oxidation and reduction. The section on fermentation remains to be published. It is almost unnecessary to inform readers of the former volumes that every serious student of enzyme chemistry will find this book essential.

While the action of hydrolytic enzymes can be studied individually *in vitro*, most biological oxidations are complex processes involving several catalysts, and their analysis is often very incomplete. Hence, the physical chemist will find pp. 76–364, which deal with the general process of respiration, rather heavy going, in spite of their excellent summary of Warburg's photochemical investigations. On the other hand, the accounts of the individual enzymes, e.g., catalase, peroxidase, and succinodehydrase, which can be studied separately, are of wider interest. Inhibition by excess of substrate is particularly characteristic of these enzymes, which may have optimum substrate concentration below 10^{-4} *M*.

Physical chemists will be interested in the discussion of Willstätter and Haber's chain reaction theory. On the other hand, they may feel that oxidation-reduction potentials might have received rather more attention.

It is perhaps inevitable that some aspects of enzyme chemistry, e.g., Moelwyn-Hughes' theory of activation, should not be touched on in this volume. We may hope for a new edition, within a few years, of the first volume of this book, in which such general problems are treated. On the other hand, students of non-biological oxidations at low temperatures will find numerous references to non-enzymatic catalysis, e.g., the oxidation of sugars in presence of heavy metal salts, that of ammo-acids in presence of charcoal and of synthetic haemochromogens, which have appeared in biological journals little read by most chemists.

While, therefore, this book is indispensable to the biochemist, the physical chemist will find that it contains valuable information on many aspects of catalysis.

J. B. S. HALDANE.

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